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Attorney Docket No. 2950.20US01

APPEAL BRIEF TRANSMITTAL

In re the application of:

Chaloner-Gill et al.

Confirmation No.: 2942

Application No.: 09/845,985

Examiner: Ruthkosky, M.

Filed: April 30, 2001

Group Art Unit: 1745

For: PHOSPHATE POWDER COMPOSITIONS AND METHODS FOR FORMING  
PARTICLES WITH COMPLEX ANIONS

Mail Stop Appeal Brief-Patents  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

Transmitted herewith, is the Appeal Brief in the above-identified application, with respect to the Notice of Appeal filed on March 13, 2007.

[ X ] Applicant(s) is/are entitled to small entity status in accordance with 37 CFR 1.27.

[ X ] A check in the amount of [ ] \$500.00 (large entity) [ X ] \$250.00 (small entity) to cover the filing fee.

Respectfully submitted,

*Peter S. Dardi*

Peter S. Dardi, Ph.D.

Registration No. 39,650

*Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.*

CERTIFICATE OF MAILING

I hereby certify that this document is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on

May 14, 2007  
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*Peter S. Dardi*  
Peter S. Dardi, Ph.D.



PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

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BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

BRIEF FOR APPELLANT



2

Application No.: 09/845,985  
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Attorney Docket No.: 2950.20US01

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BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES  
APPEAL BRIEF

Mail Stop Appeal Brief - Patents  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

INTRODUCTORY COMMENTS

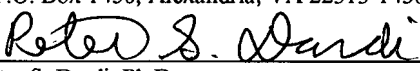
This is an appeal of the final rejection of claims 1-3, 6-9, 12, 14-21, 48-50, 52-56 and 58-61. A Final Rejection was mailed on December 13, 2006. A Notice of Appeal was filed March 13, 2007. This Appeal Brief is thus timely filed.

*Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.*

CERTIFICATE OF MAILING

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May 14, 2007  
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Peter S. Dardi, Ph.D.

**REAL PARTY IN INTEREST**

NanoGram Corporation, a corporation organized under the laws of the state of Delaware, and having offices at 165 Topaz St., Milpitas, California, has acquired the entire right, title and interest in and to the invention, the application, and any and all patents to be obtained therefore, as per the Assignment, recorded at Reel 013434, Frame 0292 from the inventors to NeoPhotonics Corporation (then named NanoGram Corporation) and an assignment from NeoPhotonics Corporation to NanoGram Corporation, recorded at Reel 013957, Frame 0076. Note that NeoPhotonics Corporation was formerly called NanoGram Corporation, and the present NanoGram Corporation was previously a wholly owned subsidiary of NeoPhotonics Corporation following the formal name change. The present NanoGram Corporation is now an independent corporation.

**RELATED APPEALS AND INTERFERENCES**

The assignee of the present application has several other applications presently on appeal. However, none of these appeals are related to the present appeal with respect to the same references. However, Appellant's pending appeal of application serial number 09/435,748 has similar issues relating to indefiniteness. Since no other decided appeals are related in any relevant way to the present appeal, no earlier opinions are attached in the Related Appeals Appendix.

**STATUS OF CLAIMS**

Claims 1-3, 6-9, 12, 14-21, 48-50, 52-56 and 58-61 are pending, and all of the pending claims stand rejected. Claims 4, 5, 10, 11, 13, 22-47, 51 and 57 have been canceled. The pending claims are listed in the Claims Appendix.

### **STATUS OF AMENDMENTS**

The Amendment After Final of February 2, 2007 has not been entered. A supplemental Amendment After Final was submitted on the same day as this Appeal Brief that only cancels claims 4, 10 and 57, which was presently inconsistent with the corresponding independent claim. Appellant assumes for the purposes of this Brief that claims 4, 10 and 57 have been canceled.

### **SUMMARY OF CLAIMED SUBJECT MATTER**

The present invention is directed to highly uniform submicron metal phosphate particles. The particles can be crystalline or amorphous. In particular, independent claims 1 and 55 are directed to crystalline particles, while independent claims 21 and 58 are directed to amorphous particles. For convenience, references to Appellant's specification will use paragraph numbers for the published application, US 2002/0192137A.

Appellant's specification describes the development of laser pyrolysis for the synthesis of particles comprising inorganic compositions with complex anions. See Appellant's specification at ¶¶ 0037, 0038, 005 and 0064. This is a significant inventive development. It is based in part on improvements in aerosol delivery developed by Appellant for laser pyrolysis, as described in U.S. Patents 6,193,936, 6,508,855, 6,607,706 and 7,029,513. In laser pyrolysis, a reactant flow passes through an intense light beam that drives the reaction to product particles. The present developments are based in part on the surprising discovery that complex anions in an aerosol precursor can survive intact or can be formed during the reaction for incorporation into the product particles. See Appellant's specification at ¶¶ 0052 and 0164-0169. Thus, the ability to form submicron, uniform particles with complex anions, such as phosphate anions provides the ability to synthesize the claimed materials.

For the crystalline particles, the claims are directed to particle collections with an average particle size of less than about a micron (claims 1 and 55), or from about 5 nm to about 250 nm

(claim 2) or from about 5 nm to about 100 nm (claims 3, 56 and 59). See Appellant's specification at ¶ 0119. The crystalline particles have a lithium cation and another metal cation in the particle. (Claims 1 and 55, see specification at ¶ 0126). In some embodiments, the particles can comprise three or more metal elements. (Claim 6 and specification at ¶¶ 0036, 0127 and 0128.) Compositions of specific interest include  $\text{Li}_x\text{FePO}_4$ ,  $0.1 \leq x \leq 1$  (claims 7 and 17),  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ,  $0 \leq x \leq 0.8$  (claim 8),  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ,  $0.4 \leq x \leq 0.8$  (claim 9) and  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ,  $0.6 \leq x \leq 0.8$  (claim 18). See specification at ¶¶ 0128 and 0134.

In particular, crystalline particles are presently desirable for use in batteries. (Claim 16) In particular, lithium batteries can provide large energy densities with either lithium metal anodes (claim 19) or lithium intercalation compounds in the anode (claim 20). See Appellant's specification at ¶ 0132.

In addition, for the amorphous particles, the average particle sizes are stated to be less than about 95 nm. (Claims 21 and 58, specification at ¶¶ 0007, 0119 and 0129.) In some embodiments, the amorphous particles have a plurality of metal elements in the particles (claims 48, 57 and 60), such as at least three metals (claim 49), and one of the metals can be lithium (claim 50). See specification, for example, at ¶¶ 0036, 0127 and 0128. Some specific compositions of interest for amorphous phosphates include  $\text{FePO}_4$  (claim 12),  $\text{AlPO}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$  (claims 54 and 61). See specification at ¶ 0129.

A significant aspect of the inventive particle collections relate to the uniformity of the particles. The uniform powders that can be produced by laser pyrolysis can have uniformities in particle size that can be described distinctly with respect to a cut off in the particle size distribution or as a sharp peak in the particle size distribution. With respect to the cut off in the particle size distribution, this can be described as there being essentially no particles with a diameter greater than about 5 times the average particle size (claims 1 and 21), or greater than about 3 times the average particle size (claims 14 and 52). See specification at ¶¶ 0122 and 0123. The cut off in the particle size distribution can be described pictorially by saying that the

powders do not have any have any "boulders," i.e. disproportionally larger particles scattered among the smaller particles of the collection. This pictorial concept expresses the idea that there are no rare massive particle within the submicron powders. The specification described the absence of particles with respect to less than 1 in a million particles. See specification at ¶ 0123.

With respect to the narrow particle size peak, this is an indication of the bulk of the particles are all within a small particle size range. In particular, at least about 95 percent of the particles have a diameter greater than 40 percent of the average diameter and less than about 160 percent of the average diameter. (Claims 53, 55 and 58, specification at ¶ 0122.) Thus, this indicates that if the plot of particle size distribution is cut off at a value of 40 percent of the average diameter at small particle sizes and at a value of 160 percent of the average diameter at large particle sizes, then the remaining portions of the curve would have an area of at least 95 percent of the area of the entire particle size distribution curve. Thus, a large majority of the particles fall within a very small particle size distribution. Claims 15 and 53 include both features of the particle size uniformity specified. Particle size uniformity is an important feature of a particle collection. To conceptualize this concept pictorially, a golf ball, a tennis ball, a baseball and a basket ball may have an average diameter approximately the same as a softball, but these ball collections have very different properties than a collection of four softball that differ only slightly from each other in size.

The uniformity of the particles as well as the quality of the crystalline particles leads to excellent battery performance. Specification at ¶¶ 0044 and 0121. Lithium metal phosphate compounds provide a high energy density, safe alternatives to some of the metal oxide powders that have resulted in overheating and fires for some laptop computer batteries in the recent news.

#### **GROUND OF REJECTION TO BE REVIEWED ON APPEAL**

1. The rejection of claims 1-4, 6-10, 12-21 and 48-61 as unpatentable under 35 U.S.C. § 112, second paragraph, as being indefinite.

2. The rejection of claims 1-4, 6, 7, 10, 12, 14-17, 19-21, 48-50, 52, 53 and 55-61 under 35 U.S.C. § 103(a) as unpatentable over U.S. 5,538,814 to Kamauchi et al. in view of U.S. 5,789,115 to Manev.

3. The rejection of claims 8, 9 and 18 under § 103(a) as unpatentable over U.S. 5,910,382 to Goodenough et al., and in further view of U.S. 5,538,814 to Kamauchi et al., and U.S. 5,789,115 to Manev.

4. The rejection of claims 54, 58, 59 and 61 under 35 U.S.C. § 103(a) as unpatentable over U.S. 5,849,827 to Bodiger et al. in view of U.S. 5,952,125 to Bi et al.

## **ARGUMENT**

### **GROUPING OF CLAIMS**

The following argument is organized around the following grouping of claims, which is summarized for the convenience of the Board.

1. Claims 1, 6-9, 14 and 16-20 fall within a first claim group directed to lithium metal phosphate particles with a submicron average particle size and a lack of particles having a diameter greater than five times the average particle diameter, which corresponds with having a uniformity expressed with a lack of a tail in the particle size distribution.

2. Claims 2 and 3 fall within a second claim group directed to crystalline lithium metal oxide particles with a smaller maximum average particle sizes.



3. Claim 15 falls within a third claim group directed to lithium metal phosphate particles with a submicron average particle size, an absence of substantially larger particles and a uniformity represented by a narrow peak in the particle size distribution.
4. Claims 12, 21, 48-50 and 52-54 fall within a fourth claim group directed to amorphous particles of a phosphate composition with an average particle size less than about 95 nm and having a lack of substantially larger particles having a diameter greater than five times the average particle diameter.
5. Claims 55-56 fall within a fifth claim group directed to crystalline lithium phosphate particles with a submicron average particle size and a uniformity in particle size represented by a narrow peak in the particle size distribution.
6. Claims 58-61 fall within a sixth claim group directed to amorphous phosphate particles with an average particle size less than about 95 nm and a uniformity in particle size represented by a narrow peak in the particle size distribution.

#### LEGAL AUTHORITY

The Court of Appeals for the Federal Circuit has exclusive appellate jurisdiction for cases arising under the patent law under 28 U.S.C. § 1295 (a)(1). Federal Circuit patent law is subject to review by the U.S. Supreme Court, and the Supreme Court occasionally rules on patent cases that provide ultimate authority for interpreting the patent statutes. The Federal Circuit has adopted as binding precedent all holding of its predecessor courts, the U.S. Court of Claims and the U.S. Court of Customs and Patent Appeals. South Corp. v. U.S., 215 USPQ 657 (Fed. Cir. 1982). Therefore, unless they have been overruled *en banc* or by the Supreme Court, CCPA cases are binding precedent for the present appeal.

#### A. INDEFINITENESS

The patent statute at 35 U.S.C. § 112, second paragraph, requires that the "specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention." "Whether a claim is invalid for indefiniteness requires a determination whether those skilled in the art would understand what is claimed when the claim is read in light of the specification." Morton International Inc. v. Cardinal Chemical Co., 28 USPQ2d 1190, 1194 (Fed. Cir. 1993). "Definiteness problems often arise when words of degree are used in a claim. That some claim language may not be precise, however, does not automatically render a claim invalid." Seattle Box CO. v. Indus. Crating & Packing, Inc., 731 F.2d 818m, 826 (Fed. Cir. 1984).

"The district court, though discussing enablement, spoke also of indefiniteness of 'stretch rate,' a matter having to do with § 112, second paragraph, and relevant in assessment of infringement. The use of stretching \* \* \* at a rate exceeding **about** 10% per second' in the claims is not indefinite. Infringement is clearly assessable through use of a stop watch." W. L. Gore & Associates, Inc. v. Garlock, Inc., 220 USPQ 303, 316 (Fed. Cir. 1983)(emphasis added). In contrast, when "the meaning of claims is in doubt, especially when ... there is close prior art, they are properly declared invalid." Amgen Inc. v. Chugai Pharmaceutical Co. Ltd., 18 USPQ2d 1016, 1031 (Fed. Cir. 1991). "In arriving at this conclusion, we caution that our holding that the term "about" renders indefinite claims 4 and 6 should not be understood as ruling out any and all uses of this term in patent claims." Id. "The meaning of the word 'about' is dependent on the facts of a case, the nature of the invention, and the knowledge imparted by the totality of the earlier disclosure to those skilled in the art." Eiselstein v. Frank, 34 USPQ2d 1467, 1471 (Fed. Cir. 1995). This last case outlines how the term "about" is generally interpreted in patent claims.

"The question becomes whether one of ordinary skill in the art would understand what is claimed when the claim is read in light of the specification." BJ Services Co. v. Halliburton

Energy Services, Inc., 338 F.3d 1368, 1372 (Fed. Cir. 2003); rehearing and rehearing *en banc* denied October 17, 2003. The court in BJ Services Co. affirmed the definiteness of "about 0.06" in the claim and affirmed that the claim was not anticipated by a value of 0.077 in the prior art. *Id.* at 1373. The court noted that the term about was "used to encompass experimental error."

The fact that scientific measurements have a certain precision associated with them has led one court to conclude that a whole number inherently has an approximate nature. See Eiselstein v. Frank, above ("Such a description indicates that Eiselstein knew how to be precise when he intended to, and supports the conclusion that otherwise, when a whole number was stated, a precise amount was not intended.").

## B. LEGAL BACKGROUND - OBVIOUSNESS

### 1. The Examiner Bears The Burden Of Demonstrating Obviousness.

The Examiner has the burden of persuasion in showing that the Appellants are not entitled to a patent. "[T]he conclusion of obviousness *vel non* is based on the preponderance of evidence and argument in the record." In re Oetiker, 24 USPQ2d 1443, 1445 (Fed. Cir. 1992). The patent office has the ultimate burden of persuasion in establishing that an applicant is not entitled to a patent. *Id.* at 1447, concurring opinion of Judge Plager. **"The only determinative issue is whether the record as a whole supports the legal conclusion that the invention would have been obvious."** *Id.*

"In rejecting claims under 35 U.S.C. §103, the examiner bears the initial burden of presenting a prima facie case of obviousness." In re Rijckaert, 28 USPQ2d 1955, 1956 (Fed. Cir. 1993). Prima facie obviousness is not established if all the elements of the rejected claim are not disclosed or suggested in the cited art. In re Ochiai, 37 USPQ 1127, 1131 (Fed. Cir. 1995). "The test for obviousness *vel non* is statutory. It requires that one compare the claim's 'subject matter as a whole' with the prior art 'to which said subject matter pertains.'"). **"It is impermissible, however,**

to simply engage in a hindsight reconstruction of the claimed invention, using applicant's structure as a template and selecting elements from references to fill the gaps." In re Gorman, 18 USPQ2d 1885, 1888 (Fed. Cir. 1991)(emphasis added).

If the Examiner fails to establish a prima facie case of obviousness, the obviousness rejection must be withdrawn as a matter of law. In re Ochiai, 37 USPQ at 1131 ("When the references cited by the examiner fail to establish a prima facie case of obviousness, the rejection is improper and will be overturned." Emphasis added.).

"To establish a *prima facie* case of obviousness, three basic criteria must be met. First, there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings. Second, there must be a reasonable expectation of success. Finally, the prior art reference (or references when combined) must teach or suggest all the claim limitations. The teaching or suggestion to make the claimed combination and reasonable expectation of success must both be found in the prior art, and not based on applicant's disclosure. *In re Vaeck*, 947 F.2d 488, 20 USPQ2d 1438 (Fed. Cir. 1991)." MPEP 2142.

## 2. Differences Between The Scope Of The Prior Art And The Claimed Invention Must Be Evaluated

The two initial factual determinations under a Graham analysis of obviousness mandated by the Supreme Court are (A) Determining the scope and content of the prior art and (B) Ascertaining the differences between the prior art and the claims at issue. See MPEP 2141 citing Graham v. John Deere, 383 U.S. 1, 148 USPQ 459 (1966). The "factors [recited in Graham] continue to define the inquiry that controls." KRS Int'l Co. v. Teleflex Inc., 550 U.S. \_\_\_\_ (2007) Slip. Op. at 2. In evaluating the differences between the prior art and the claimed invention, the invention as a whole must be considered. See MPEP 2141.02 citing Stratoflex, Inc. v. Aeroquip Corp. 218 USPQ 871 (Fed. Cir. 1983). Similarly, a prior art reference must be considered "as a

whole, including portions that would lead away from the claimed invention." See MPEP 2141.02 (emphasis in original) citing W. L. Gore & Associates, Inc. v. Garlock, Inc., 220 USPQ 303 (Fed. Cir. 1983), cert. denied, 469 U.S. 851 (1984). Under Graham, the evaluation of the teachings is performed from the perspective of a person of ordinary skill in the art. "A person of ordinary skill is also a person of ordinary creativity, not an automaton." KRS Int'l Co., 550 U.S. at \_\_\_, Slip Op. at 17.

3. There Must Be Motivation In The Art To Modify The Teachings Of the Cited References

The motivation, or suggestion, to modify the teachings of a reference must be either explicitly or implicitly in the references or knowledge "generally available to one of ordinary skill in the art." See, MPEP § 2143.01. Furthermore, "[t]he test for an implicit showing [of motivation] is what the combined teachings, knowledge of one of ordinary skill in the art, and nature of the problem to be solved as a whole would have suggested to those of ordinary skill in the art." See, MPEP §2143.01 (quoting In re Kotzab, 55 USPQ2d 1313, 1317 (Fed. Cir. 2000)).

Referring to MPEP 2143.01, it is well established that **"Fact that References Can Be Combined Or Modified Is Not Sufficient To Establish *Prima Facie* Obviousness."** Furthermore, referring to MPEP 2143 "The teaching or suggestion to make the claimed combination and the reasonable expectation of success must be both found in the prior art, and not based on applicant's disclosure." Citing In re Vaeck, 20 USPQ2d 1438 (Fed. Cir. 1991).

The Supreme Court has recently clarified that this examination of the teachings of the prior art should not be performed rigidly. Specifically, "a court must ask whether the improvement is more than the predictable use of prior art elements according to their established functions." KSR Int'l Co., 550 U.S. at \_\_\_, Slip Op. at 13. "Often, it will be necessary for a court to look to interrelated teachings of multiple patents; the effects of demands known to the design community or present in the marketplace; and the background knowledge possessed by a

person of ordinary skill in the art, all in order to determine whether there was an apparent reason to combine the known elements in the fashion claimed by the patent at issue." *Id.* at \_\_\_, Slip Op. at 14. The Court noted that "it can be important to identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements in the way the claimed new invention does. This is so because inventions in most, if not all, instances rely upon building blocks long since uncovered, and claimed discoveries almost of necessity will be combinations of what, in some sense, is already known." *Id.* at \_\_\_, Slip Op. at 15. "Under the correct analysis, any need or problem known in the field of endeavor at the time of invention and addressed by the patent can provide a reason for combining the elements in the manner claimed." *Id.* at \_\_\_, Slip Op. at 16.

The Federal Circuit has provided considerable guidance on establishing obviousness of a claim. "Our case law makes clear that the best defense against hindsight-based obviousness analysis is the rigorous application of the requirement of a teaching or motivation to combine the prior art references." *Ecolochem Inc. v. Southern Edison*, 56 USPQ2d 1065, 1073 (Fed. Cir. 2000). "Therefore, '[w]hen determining the patentability of a claimed invention which combines two known elements, 'the question is whether there is something in the prior art as a whole to suggest the desirability, and thus the obviousness, of making the combination.' " *Id.* (quoting *In re Beattie*, 24 USPQ2d 1040, 1042 (Fed. Cir. 1992)(quoting *Lindemann Maschinenfabrik GmbH v. American Hoist and Derrick Co.*, 221 USPQ 481, 488 (Fed. Cir. 1984))). The Supreme Court has confirmed the warnings in *Graham* against hindsight analysis by noting that a "factfinder should be aware, of course, of the distortion caused by hindsight bias and must be cautious of arguments reliant upon *ex post* reasoning." *KSR Int'l Co.*, 550 U.S. at \_\_\_, Slip Op. at 17.

The importance of the principle that the prior art itself must suggest the motivation to modify the teachings of a reference was eloquently stated in *In re Rouffet*, 47 USPQ2d 1453, 1458 (Fed. Cir. 1998)(emphasis added):

The Board did not, however, explain what specific understanding or technical principle within the knowledge of one of ordinary skill in the art would have suggested the combination. **Instead the board merely invoked the high level of skill in the field of the art. If such a rote invocation could suffice to supply a motivation to combine, the more sophisticated scientific fields would rarely, if ever, experience a patentable technical advance.** Instead, in complex scientific fields, the Board could routinely identify the prior art elements in an application, invoke the lofty level of skill, and rest its case for rejection. **To counter this potential weakness in the obviousness construct, the suggestion to combine requirement stands as a critical safeguard against hindsight analysis and rote application of the legal test for obviousness.**

"There is no suggestion to combine [references] if a reference teaches away from its combination with another source." *Tec Air Inc. v. Denso Manufacturing Michigan Inc.*, 52 USPQ2d 1294, 1298 (Fed. Cir. 1999). "A reference will teach away if it suggests that a line of development flowing from the reference's disclosure is unlikely to be productive of the result sought by the applicant." *Winner International Royalty Corp. v. Wang*, 53 USPQ2d 1580, 1587 (Fed. Cir. 2000)(quoting *In re Gurley*, 31 USPQ2d 1130, 1131 (Fed. Cir. 1994)). "A reference may be said to teach away when a person of ordinary skill, upon reading the reference, would be discouraged from following the path set out in the reference, or would be led in a direction divergent from the path that was taken by the applicant." *In re Gurley*, 31 USPQ2d 1130, 1131 (Fed. Cir. 1994).

#### 4. The References Must Teach Or Suggest All Of The Claim Elements

Prima facie obviousness is not established if all the elements of the rejected claim are not disclosed or suggested in the cited art. *In re Ochiai*, 37 USPQ 1127, 1131 (Fed. Cir. 1995). ("The test for obviousness *vel non* is statutory. It requires that one compare the claim's 'subject matter as a whole' with the prior art 'to which said subject matter pertains.'"). See also, MPEP 2143.03 "All Claim Limitations Must Be Taught or Suggested," citing *In re Royka*, 180 USPQ 580 (CCPA 1974). **"To establish prima facie obviousness of a claimed invention, all of the claim limitations must be taught or suggested by the prior art."** MPEP 2143.03.

To establish prima facie obviousness, all the elements of the claim must be taught or suggested by the cited references without the benefit of hindsight based on the applicant's own disclosure. "To imbue one of ordinary skill in the art with knowledge of the invention in suit, when no prior art reference or references of record convey or suggest that knowledge, is to fall victim to **the insidious effect of a hindsight syndrome** wherein that which only the inventor taught is used against its teacher." W. L. Gore & Assocs., Inc. v. Garlock, Inc., 220 USPQ 303, 312-13 (Fed. Cir. 1983). **"Skill in the art does not act as a bridge over gaps in the substantive presentation of an obviousness case, but instead supplies the primary guarantee of objectivity in the process."** All-Site Corp. v. VSI International Inc., 50 USPQ2d 1161, 1171 (Fed. Cir. 1999)(emphasis added).

5. The References Must Provide A Reasonable Expectation Of Success

While a reference is prior art for all that it teaches, references along with the knowledge of a person of ordinary skill in the art must be enabling to place the invention in the hands of the public. In re Paulsen, 31 USPQ2d 1671, 1675 (Fed. Cir. 1994). See also In re Donohue, 226 USPQ 619, 621 (Fed. Cir. 1985). "The consistent criterion for determination of obviousness is whether the prior art would have suggested to one of ordinary skill in the art that this process should be carried out and would have a reasonable likelihood success, viewed in light of the prior art." Micro Chemical Inc. v. Great Plains Chemical Co., 41 USPQ2d 1238, 1245 (Fed. Cir. 1997)(quoting In Re Dow Chemical Co., 5 USPQ2d 1529, 1531 (Fed. Cir. 1988)).

ANALYSIS

Rejection Under 35 U.S.C. § 112

The Examiner rejected claims 1-4, 6-10, 12-21 and 48-61 under 35 U.S.C. § 112, second paragraph as being indefinite. The Examiner asserts on page 2 of the final Office Action that "less than" and "greater than" describe definite "maximum" and "minimum" values respectively that are contradicted by the term "about." The Examiner made similar assertions regarding "at



least about." As an initial matter, the Examiner stated on page 2 of the office action that as "shown in the MPEP, section 2173.05(b), section (a), the phrase 'at least about' is held indefinite." With all due respect, the MPEP does not say quite what the Examiner indicated. MPEP 2173(b)(A) also indicates specific situations in which a claim with the term "about" is clear in the particular context. In particular, indefiniteness is examined from the point of view of a person of ordinary skill in the art. See the general discussion of case law above. The Examiner has fallen very short of establishing *prima facie* indefiniteness. Appellant respectfully requests consideration of the following arguments.

The patent statute at 35 U.S.C. § 112, second paragraph, requires that the "specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention." "Whether a claim is invalid for indefiniteness requires a determination whether those skilled in the art would understand what is claimed when the claim is read in light of the specification." Morton International Inc. v. Cardinal Chemical Co., 28 USPQ2d 1190, 1194 (Fed. Cir. 1993).

The Examiner relies on the Amgen case. In particular, when "the meaning of claims is in doubt, especially when ... there is close prior art, they are properly declared invalid." Amgen Inc. v. Chugai Pharmaceutical Co. Ltd., 18 USPQ2d 1016, 1031 (Fed. Cir. 1991). "In arriving at this conclusion, **we caution that our holding that the term "about" renders indefinite claims 4 and 6 should not be understood as ruling out any and all uses of this term in patent claims.**" Id. (emphasis added). "The meaning of the word 'about' is dependent on the facts of a case, the nature of the invention, and the knowledge imparted by the totality of the earlier disclosure to those skilled in the art." Eiselstein v. Frank, 34 USPQ2d 1467, 1471 (Fed. Cir. 1995). This last case outlines how the term "about" is generally interpreted in patent claims. In a recent Federal Circuit case, the court affirmed a jury finding that "about 0.06" was not indefinite and that a prior art value of "0.077" did not anticipate the value of "about 0.06." B.J. Services Co. v. Halliburton Energy Services, Inc., 338 F.3d 1368 (Fed. Cir. 2003).

The fact that scientific measurements have a certain precision associated with them has led one court to conclude that **a whole number used to approximate a continuous variable** inherently has an approximate nature. See Eiselstein v. Frank, above ("Such a description indicates that Eiselstein knew how to be precise when he intended to, and supports the conclusion that otherwise, when a whole number was stated, a precise amount was not intended.").

While Appellant specifically asked the Examiner to identify a person of ordinary skill in the art in the Amendment of June 14, 2005, the Examiner did not identify such a person of skill in the art. ("Applicants respectfully request that the Examiner explain who is being described as a person of ordinary skill in the art and why such a person would not understand this simple language.") Appellant asserts that a person of ordinary skill in the art would be a Ph.D. scientist or engineer in materials or battery technology.

A person of ordinary skill in the art would recognize that in the real world exact values of real non-integer numbers are meaningless. Scientists put error bars on their measurements. Measurements of values necessarily have an associated precision. It is very clear that a person of ordinary skill in the art would recognize immediately that the term "about" reflects this necessary imprecision in the measurements.

It is well established in the case law that the term "about" is interpreted in a claim based on the particular facts of the case. Similarly, the case law has acknowledged the clear fact that continuous variables have a precision associated with them that inherently introduces a range of meaning to a particular number. Thus, a number does not have precise meaning with respect to a continuous variable. Thus, if an object is stated to be 10 inches long, this clearly really means that it is 10 inches +/- some precision related to the measurement in the particular art field. See, e.g., Eiselstein v. Frank, supra.

In summary, the use of the term "about" reflects the natural imprecision in expressing continuous variables with approximate cut off values at a particular precision. This is particularly true with respect to nanotechnology where measurement has particularly clear complications. On a

nano-scale, the meaning of the term "about" is related to the capabilities for measurement of the particular characteristic at the time in which the application was filed. Thus, Applicants' claims are clear to a person of ordinary skill in the art at filing.

With all due respect, Applicants have searched the PTO web site and have found since 1976 there have been **53,976** patents issued with the phrase "less than about" in their claims. Many of these have been issued recently. Similarly, **28,519** patents have issued since 1976 with the phrase "greater than about" in their claims. Either there are countless incompetent patent examiners, which Applicants do not believe is true, or the phrase is not inherently indefinite. Applicants have argued case law and the perspective of an ordinary person of skill in the art. The Examiner has failed to assert why in the present context that the phrases are unclear. Furthermore in Europe, "about" is accepted in claims relating to the nanoscale. See, for example, EP 1 027 400B and EP 1 027 819B.

In view of Applicants' arguments that the PTO has allowed many other applications with the offending language, the Examiner asserts that there is close prior art that precludes the current language. With respect to the claimed subject matter as a whole, **the prior art is simply not close**. No references teach or suggest the claimed materials with the claimed average particles sizes and the claimed **particle size distributions** which correspond with highly uniform materials. There is no close prior art in the average particle size range with respect to **uniform** submicron phosphate compositions.

Since a person of ordinary skill in the art can evaluate the meaning of the claims, the Examiner has not established prima facie indefiniteness of the claims. Applicants respectfully request withdrawal of the rejection of claims 1-4, 6-10, 12-21 and 48-54 under 35 U.S.C. § 112, second paragraph, as being indefinite.

### Rejection Over Kamauchi et al. and Manev

The Examiner rejected claims 1-4, 6, 7, 10, 12, 14-17, 19-21, 48-50, 52, 53 and 55-61 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent 5,538,814 to Kamauchi et al. (the Kamauchi patent, see Evidence Appendix) in view of U.S. Patent 5,789,115 to Manev (the Manev patent, see Evidence Appendix). Appellant maintains that the Examiner has fallen far short of establishing *prima facie* obviousness. Assuming *arguendo* that the Examiner had established *prima facie* obviousness, Appellant has presented un-refuted evidence relating to patentability. Furthermore, Appellant discusses other objective evidence of non-obviousness below. Appellant respectfully requests reconsideration of the rejection based on the following comments.

### General Arguments for All Claim Groups

Prima facie obviousness is not established if all the elements of the rejected claim are not disclosed or suggested in the cited art. In re Ochiai, 37 USPQ 1127, 1131 (Fed. Cir. 1995). ("The test for obviousness *vel non* is statutory. It requires that one compare the claim's 'subject matter as a whole' with the prior art 'to which said subject matter pertains.'"). See also, MPEP 2143.03 "All Claim Limitations Must Be Taught or Suggested," citing In re Royka, 180 USPQ 580 (CCPA 1974). **"To establish prima facie obviousness of a claimed invention, all of the claim limitations must be taught or suggested by the prior art."** MPEP 2143.03.

The Examiner admits on page 4 of the final Office Action that the Kamauchi patent does not teach the claims particle size uniformity. Thus, the Examiner cites the Manev patent with respect to teachings related to this feature of Appellant's claimed invention. In particular, the Examiner refers to column 1, lines 34-50 of Manev. There are several serious shortcomings of this argument.

First, Manev relates only to lithium metal oxides and not to metal phosphate compositions. The rationale given by Manev with respect to small particles and uniform particle size distribution relates to an "increase in cyclability" since "smaller particles are relatively more flexible than larger particles and therefore the changes in the crystal lattice parameters which occur during cycling do not damage the cyclability of the smaller particles to the degree that the larger particles are damaged." It is not clear that these principles apply to phosphates, which have a phosphate anion in the crystal lattice. Furthermore, it has been found that nano-scale particles are less able generally to accommodate crystalline defects that can complicate intercalation of lithium atoms into the lattice. On the other hand, phosphates are known to have increased inherent stability during cycling. See Striebel article in the evidence appendix. Perhaps this improved cycling is due to the larger size of the phosphate anion. Thus, the desirable properties of phosphate submicron particles were unexpected in the application of secondary batteries.

Also, neither the Manev patent nor the Kamauchi patent teach a submicron powder with particles having the claimed uniformity. In particular, the Manev patent teaches uniform particles having an average particle size greater than a micron, while Kamauchi teaches arguably small particles, but with no efforts to have the claimed uniformity. Thus, the references alone or combined do not teach particles with an average submicron particle size with the claimed uniformity for any material. The MPEP makes it clear that the claim limitations must be taught by the references.

As the Supreme Court has mandated with respect to a correct analysis, "any need or problem known in the field of endeavor at the time of invention and addressed by the patent can provide a reason for combining the elements in the manner claimed." KRS Int'l Co., 550 U.S. at \_\_\_, Slip Op. at 16. However, Manev teaches away from the combination suggested by the Examiner. Specifically, Manev explicitly teaches that the particles should not be made too small. In particular, Manev teaches that the powders should have an average particle size greater

than a micron and preferably greater than 5 microns. Specifically, at column 4, lines 64-67, Manev teaches that the lithium manganese oxides have the same particle size distributions roughly as the "starting manganese compound." At column 3, lines 37-61, Manev states that the "manganese compound has a predetermined mean particle diameter of between about 1 and 15 microns, preferably between greater than 1 and 15 microns and more preferably between about 5 and 15 microns." In addition, referring to column 1, lines 50-67, Manev states the following.

**"Nevertheless, a decrease in the mean particle size results in a significant increase in the electronic resistivity of the spinel compounds.** The electronic resistivity is controlled by the contact resistivity between the particles which rises significantly due to an increase in the number of contact boundaries which the electrons have to overcome. The increase in electronic resistivity leads to an increase in the electronic polarization which decreases the specific capacity and the charge-discharge rate capability of the electrode. Furthermore, **a decrease in the particle size is generally coupled with an unwanted decrease in the tapped or powder density.** Because many batteries such as batteries for electronics have fixed volumes, it is preferred that the spinel material used in the positive electrode of these batteries has a high tap density, so there is essentially more chargeable material in the positive electrode. A higher tap density results in a positive electrode having a higher overall capacity."

Since Manev teaches that the particles should have an average particle size of greater than a micron for lithium metal oxide particles, Manev simply does not teach or suggest uniform submicron metal phosphate particles. A review of the "interrelated teachings" of the patents, as suggested by the Supreme Court in KRS, indicates that the teachings of the references do not point to uniform, submicron metal phosphate particles as disclosed and claimed by Appellants.

Furthermore, while a reference is prior art for all that it teaches, references along with the knowledge of a person of ordinary skill in the art must be enabling to place the invention in the hands of the public. In re Paulsen, 31 USPQ2d 1671, 1675 (Fed. Cir. 1994). See also In re Donohue, 226 USPQ 619, 621 (Fed. Cir. 1985). "The consistent criterion for determination of obviousness is whether the prior art would have suggested to one of ordinary skill in the art that this process should be carried out and would have a reasonable likelihood success, viewed in light of the

prior art." Micro Chemical Inc. v. Great Plains Chemical Co., 41 USPQ2d 1238, 1245 (Fed. Cir. 1997)(quoting In Re Dow Chemical Co., 5 USPQ2d 1529, 1531 (Fed. Cir. 1988)).

The proposition is well established that the cited art only renders a composition of matter or apparatus unpatentable to the extent that the cited art enables the disputed claims, in other words, if the cited art provides a means of obtaining the claimed composition or apparatus.

To the extent that anyone may draw an inference from the Von Bramer case that the mere printed conception or the mere printed contemplation which constitutes the designation of a 'compound' is sufficient to show that such a compound is old, regardless of whether the compound is involved in a 35 U.S.C. 102 or 35 U.S.C. 103 rejection, we totally disagree. ... We think, rather, that the true test of any prior art relied upon to show or suggest that a chemical compound is old, is whether the prior art is such as to place the disclosed 'compound' in the possession of the public. In re Brown, 141 USPQ 245, 248-49 (CCPA 1964)(emphasis in original)(citations omitted).

The Kamauchi patent teaches milling as an approach to form submicron metal phosphate particles. However, there are significant shortcomings to the teachings of Kamauchi in this regard. First, it is noted that Kamauchi defines particle size with respect to powder surface area. Techniques to measure powder surface area involve gas sorption on the particles. However, it is well known to persons of ordinary skill in that art that highly porous particles can have large gas sorption while the particles are not correspondingly small. For example, U.S. Patent 4,105,426 to Iler et al. in Table I teaches particles with average diameter of 6 microns with a surface area of 271 m<sup>2</sup>/g, and U.S. Patent 6,747,113 to Spencer et al. at column 14 teaches particles with an average particle size of 145 microns with a surface area of 310 m<sup>2</sup>/g, which are in the ranges of the surface areas disclosed by Kamauchi. Thus, measured surface areas only correlate with average particle size for non-porous particles. As noted in column 2 of Manev, milling tends to fragment particles and destroy particle morphology. This is especially true for the excessive milling described in Examples 11 and 12 of Kamauchi. Thus, the particles described in Examples 11 and 12 of Kamauchi are very likely highly porous larger particles. In contrast,

Appellant's specification indicates that particle sizes are measures with Transmission Electron Micrographs. Thus, it is not even clear that Kamauchi teaches submicron average particle sizes as measured by TEM micrographs, at all.

The Manev patent has several severe deficiencies with respect to the proposed combination. For example, the Manev patent teaches the formation of lithium manganese oxide particles with a particle size of greater than a micron. Also, Manev teaches away from the use of milling. The compositions in Manev are formed from solid state reactions starting with manganese oxide materials, see column 3, lines 33-63. The Manev patent explicitly indicates that the manganese reactant compositions can be milled **prior to** reacting the composition to form the lithium composition. See column 4, lines 3-5. However, Manev explicitly teaches that it is undesirable to mill the electrode active material. See column 2, lines 17-20. Thus, Manev explicitly teaches away from its combination with the Kamauchi patent with respect to milling electrode active compositions since such milling degrades resulting battery performance. Furthermore, Manev teaches that the particles should not necessarily be too small. See column 1, lines 50-67. This is based on a predicted decrease in performance for smaller particles. Since Kamauchi **only teaches milling** to form their submicron materials, and Manev teaches that milling to reduce particle size is undesirable and submicron particles are undesirable, the cited references clearly do not render the claimed electrode active compositions *prima facie* obvious.

Furthermore, Appellant has submitted a 132 Declaration (see Evidence Appendix) that addresses the issue of milling as taught in the Kamauchi patent. Applicants note that the 132 Declaration provides experimental results that confirm Applicants' assertions that the grinding approaches described in the Kamauchi patent do not produce particles with the uniformity of the particle collections covered under Applicants' pending claims. This objective evidence is not explicitly contrary to any teaching in the Kamauchi patent itself.

The Examiner has not provided any evidence that the procedures taught in the Kamauchi patent are suitable for forming the claimed particle size uniformity. It is the Examiner's burden



to assert a credible basis for there being a reasonable expectation of success in order to establish *prima facie* obviousness. Appellant respectfully requested some evidence to support this critical assertion, yet the Examiner ignored this request. Furthermore, Appellant obtained experimental data relating to the process of the Kamauchi patent and submitted a Declaration based on these experiments. This Declaration is attached in the evidence appendix. This evidence remains un-refuted and provides very clear evidence supporting patentability.

With respect to secondary considerations, on page 12 of the final Office Action, the Examiner acknowledged that Applicants submitted two articles showing that an "electrode with uniform submicron particle sizes have improved rate performance in a battery." See Striebel et al. article and Delacourt et al. article in Evidence Appendix. The Office Action further states that this "is exactly what is taught in Manev (col. 1, lines 40-55) and is the basis for motivation for using the particles of Kamauchi in this distribution range." With all due respect, this is incorrect with respect to Manev. Manev at column 1, lines 50-67 teaches that the particles should not be submicron and that the particles will lose performance if the particles are submicron. Plus Manev is directed specifically to specific metal oxide compositions.

Applicants were the first to develop a new important material that has significant potential for lithium based rechargeable batteries. Appellant has obtained excellent battery performance and are working to further optimize performance. Unless Appellant can obtain appropriate protection for their inventive activities, it will be difficult or impossible to obtain funding to advance this work to the commercial level, and the public will be deprived of the opportunity to have this potential source of a valuable material. Such stifling of the rewards of creative work will seriously harm the economy. Appellant is seeking appropriate relief through this appeal to rectify this situation. While the improper granting of patents can also result in harm, there are appropriate channels to rectify this situation, such as reexaminations. The Patent Office simply does not and will not have the resources to perform a perfect job at their evaluation, but their review of applications should be based on a fair reading of the evidence and

not on some obsessive desire to limit arbitrarily the grant of patents. With all due respect, Appellant maintains that the present record has clearly supported the grant of a patent for this application for a long stretch of this prosecution, and the delay in this process has wasted valuable resources of Appellant and the Patent Office.

In summary, the Examiner has failed to establish a teaching of the claim features in the cited reference and in particular particle collections with an average size less than a micron in combination with high uniformity in particle size. Also, the Examiner has failed to establish that teachings in the art pointing to the combination of the claimed particle properties, especially since Manev teaches away from Appellant's claimed composition through the direct assertions that it is undesirable to have particles with an average particle size less than a micron. In addition, the Examiner has failed to reasonably assert grounds for of a reasonable expectation of success, the Examiner has fallen far, far short of establishing a *prima facie* showing of obviousness. Applicants maintain that the Examiner has failed to establish a case of *prima facie* obviousness. However, to the extent that *prima facie* obviousness has been established, this has been rebutted by clear objective evidence in the form of the attached 132 Declaration. **The grinding approach of Kamauchi simply does not work to produce the claimed material as demonstrated by Appellants.** Thus, the cited references simply do not teach how to produce the claimed materials. Furthermore, Applicants have presented results of surprising improved battery performance from nanoparticles of lithium iron phosphate.

Group 1 - Claims 1, 4, 6-9, 14 and 16-20

In this claim group, the uniformity is expressed with respect to "essentially no particles having a diameter greater than about 5 times the average diameter." The cited references do not teach this property for any particle collections having an average particle size less than about 1 micron. Specifically, the Manev patent teaches that most preferred particle sizes have an average,

i.e., mean, particle diameter between 5 and 15 microns, which is significantly larger than the claimed particle sizes. See, column 3, lines 57-61.

#### Group 2 - Claims 2 and 3

These claims have lower average particle sizes. These ranges of particle sizes are far from the suitable ranges of average particles sizes taught in Manev. Therefore, these claims are more clearly distinct from the teachings in Manev, such that the combination of Manev and Kamauchi even more clearly does not render the claims of Group 2 *prima facie* obvious.

#### Group 3 - Claim 15

This claim is directed to particle collections having both an effective maximum particle size from Group 1 as well as a narrow peak size. Manev does not describe this property with respect to the particle size distributions. Manev only indicates that at least about 99% of the particles have a size less than about 40 microns. See, column 3, lines 57-67. Therefore, Appellant's claimed narrow particle size property is not taught in any of the references, and this claim is even more clearly not rendered *prima facie* obvious by the cited references.

#### Group 4 - Claims 12, 21, 48-50 and 52-54

These claims are directed to amorphous phosphor particles with an average particle size of less than 95 nm. This average particle size range is far from the ranges taught in the Manev patent such that Manev even more clearly teaches away from the claimed materials. Furthermore, Manev is limited to crystalline spinel compounds such that it is not particularly relevant to these claims. Thus, there is even farther from a reasonable expectation of success provided by the teaching of the cited references. Therefore, the claims of Group 4 are even more clearly not rendered *prima facie* obvious by the combined teachings of Kamauchi and Manev.

Group 5 - Claims 55-57

As with the claims of Group 3, these claims are directed crystalline submicron phosphate particles with a narrow particle distribution peak. This narrow distribution is also discussed above in the context of Group 2 claims. Neither reference discloses a particle size distribution that meets this claim limitation relating to the narrow peak in particle size distribution. Therefore, since all of the elements are not taught at all in the cited references, this claim is clearly not rendered *prima facie* obvious by the combined teachings of Manev and Kamauchi.

Group 6 - Claims 58-61

These claims are directed to amorphous phosphate particles having an average particle size less than about 95 nm. The particle collections under these claims also have the narrow particle size distribution described with respect to Groups 2 and 5 above. Since Manev even more clearly teaches away from average particle sizes in this claimed range and since neither reference describes particle uniformity with a narrow peak as specified in these claims, the combined teachings of Kamauchi and Manev very clearly do not render these claims *prima facie* obvious.

Summary

In summary, since the cited references do not come close to establishing *prima facie* obviousness of Appellant's claimed invention and since clear evidence has been presented to support patentability, Appellant respectfully requests withdrawal of the rejection of claims 1-4, 6, 7, 10, 12, 14-17, 19-21, 48-50, 52, 53 and 55-61 under 35 U.S.C. § 103(a) as being unpatentable over the Kamauchi patent in view of the Manev patent.

Rejection Over Kamauchi et al. Manev et al. and Goodenough et al.

The Examiner rejected claims 8, 9 and 18 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent 5,910,382 to Goodenough et al. (the Goodenough patent, see Evidence

Appendix) in view of the Kamauchi patent and the Manev patent as applied to the corresponding independent claims. The deficiencies of the Kamauchi patent and the Manev patent are described in detail above. The Goodenough patent does not make up for the deficiencies of the Kamauchi patent and the Manev patent described in detail above. In particular, the Goodenough patent does not teach or suggest anything about average particle size or particle size uniformity with respect to electrode active compositions. Therefore, the combined teachings of the Kamauchi patent, the Manev patent and the Goodenough patent do not render claims 8, 9 and 18 *prima facie* obvious. Applicants respectfully request withdrawal of the rejection of claims 8, 9 and 18 under 35 U.S.C. § 103(a) as being unpatentable over the Goodenough patent in view of the Kamauchi patent and the Manev patent as applied to the corresponding independent claims.

Rejection Over Bodiger et al. and Bi et al.

The Examiner rejected claims 54, 58, 59 and 61 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent 5,849,827 to Bodiger et al. (the Bodiger patent, Evidence Appendix) in view of U.S. Patent 5,952,125 to Bi et al. (the Bi patent, Evidence Appendix). The Examiner admitted that the Bodiger patent is silent with respect to the amorphous state of the powders as well as to the uniformity of the particles, as disclosed and claimed by Appellants. The Examiner cited the Bi patent for teaching uniform materials. With all due respect, Applicants respectfully assert that the Examiner has fallen far short of establishing *prima facie* obviousness. Applicants respectfully request reconsideration of the rejections based on the following comments.

"To establish a prima facie case of obviousness, three basic criteria must be met. First, there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings. Second, there must be a reasonable expectation of success. Finally, the prior

art reference (or references when combined) must teach or suggest all the claim limitations. The teaching or suggestion to make the claimed combination and reasonable expectation of success must both be found in the prior art, and not based on applicant's disclosure." MPEP § 2142 (citing In re Vaeck, 947 F.2d 488, 20 USPQ2d 1438 (Fed. Cir. 1991)). The Supreme Court in the KSR Int'l decision did not fundamentally change these, although they mandated a flexible review of the motivation issue. See legal summary above.

With all due respect, the rejection generally has many levels of deficiencies. For example, neither reference teaches how to make nanoscale phosphates. Bodiger does refer to aluminum phosphates at column 7, line 33. But Bodiger does not exemplify nano-scale phosphates or provide a reference to a source of these materials.

Furthermore, the Bi patent does not teach how to make inorganic particles with any complex anions. Thus, while the Bi patent teaches laser pyrolysis, it simply does not teach or suggest formation of metal phosphate powders. More particularly, the Bi patent does not give any clues on how to synthesize phosphates. In fact, the present application provides the surprising result that phosphate anions in the reactant stream of a laser pyrolysis reactor can survive into the product compositions. This was not predictable nor suggested prior to the work described in the present application. This surprising result provides a significant advance in laser pyrolysis technology.

Thus, the combined teachings of the references do not place the claimed materials in the hands of the public. Specifically, Bodiger does not teach any source for nano-scale phosphates and the Bi patent does not teach how to synthesize phosphates. The only phosphate compound described at all in either reference is aluminum phosphate. Applicants could not find any description of metal phosphates generally in the cited references.

The Examiner stated that "It would be obvious to one of ordinary skill in the art at the time that the invention was made to prepare a mixture with essentially no particle with a diameter greater than about 3 or 5 times the average particle size OR that at least about 95

percent of the particles have a diameter greater than about 40 percent and less than about 160 percent of the average diameter, as one of ordinary skill in the art would recognize that when a desired average diameter is disclosed in the prior art, choosing particles close to that diameter would be desirable for the function described in the reference." With all due respect, this does not follow at all from the knowledge in the art. The Bodiger reference teaches only average particle sizes. The reference says nothing at all about the desired uniformity of the materials. The Bodiger patent describes a surprising and not understood reduction in burn times due to the inclusion of the inorganic particles. See column 1, lines 51-56. For all that is known, a broad distribution in particle sizes is needed to obtain this behavior. The Examiner's broad statement to the contrary is certainly not a suggestion in the art that flame retardants would benefit from more uniform particles. Furthermore, the reference certainly does not suggest how such uniform materials could be obtained. Thus, there is simply no teaching of all of the claim elements, and the Bodiger patent does not provide a reasonable expectation of success.

The Bi patent does not teach how to make inorganic phosphate particles or any other particles with complex, multi-atom, anions. Thus, the Bi patent does not place the presently claimed uniform phosphate particles in the hands of the public. In this regard, the Bi patent does not make up for the deficiencies of the Bodiger patent. Also, the Bi patent does not describe the desirability of uniform nanoscale phosphate particles. There is absolutely nothing in the references that would suggest in any way to combine the references as suggested by the Examiner.

The Examiner at page 9 of the final Office Action "notes that optimization of ranges within prior art conditions or through routine experimentation is not inventive." First, there is no range that is optimized in reaching Appellant's claimed material. Second, the synthesis of the materials is not based on prior art conditions. Third, nothing in the prior art suggests how to make these materials so that it is certainly NOT routine experimentation. There is nothing

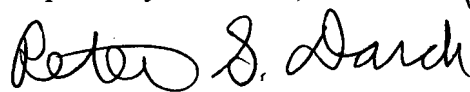
whatsoever routine about the work described in the present application, and it is certainly inventive contrary to the Examiner's conclusory statements to the contrary.

In summary, the Bodiger patent and the Bi patent alone or combined fail to teach, suggest or provide a reasonable expectation of success with respect to the claimed particle size uniformity. With all due respect, the Examiner has fallen short of establishing *prima facie* obviousness of Applicants' claimed invention over the Bodiger patent in view of the Bi patent. Applicants respectfully request withdrawal of the rejection of claims 54-56, 58, 59 and 61 under 35 U.S.C. § 103(a) as being unpatentable over the Bodiger patent in view of the Bi patent.

### CONCLUSIONS

Applicants submit that the pending claims are not rendered prima facie obvious over the combined teachings of the cited references. Applicants believe that the Patent Office has failed to meet their burden of persuasion with respect to unpatentability of any of the claims on the present record. Thus, Applicants Respectfully request the reversal of the rejections of claims 1-4, 6-9, 12, 14-21, 48-50 and 52-61.

Respectfully submitted,



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## CLAIMS APPENDIX

### LISTING OF CLAIMS ON APPEAL FOR 09/845,985

1. A collection of particles comprising a crystalline composition with a phosphate anion and a lithium cation, the collection of particles having an average particle size less than about 1000 nm and having essentially no particle with a diameter greater than about 5 times the average particle size.
2. The collection of particles of claim 1 having an average particle size from 5 nm to about 250 nm.
3. The collection of particles of claim 1 having an average particle size from 5 nm to about 100 nm.
4. The collection of particles of claim 1 having a plurality of metals in the composition.
5. (Canceled)
6. The collection of particle of claim 1 having at least three metals within the composition.
7. The collection of particles of claim 1 wherein the composition comprises  $\text{Li}_x\text{FePO}_4$ ,  $0.1 \leq x \leq 1$ .
8. The collection of particles of claim 1 wherein the composition comprises  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ,  $0 \leq x \leq 0.8$ .
9. The collection of particles of claim 1 wherein the composition comprises  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ,  $0.4 \leq x \leq 0.8$ .

10. The collection of particles of claim 1 wherein the composition comprises  $M_xPO_4$ , wherein M is a metal, x is a rational number and  $x \leq 4$ .
11. (Canceled)
12. The collection of particles of claim 21 wherein the composition comprises  $FePO_4$ .
13. (Canceled)
14. The collection of particles of claim 1 having essentially no particle with an diameter greater than about 3 times the average particle size.
15. The collection of particles of claim 1 having a distribution of particle sizes such that at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.
16. A battery comprising a cathode, the cathode comprising the collection of particles of claim 1, the particles comprising lithium metal phosphate.
17. The battery of claim 16 wherein the lithium metal phosphate comprises  $Li_xFePO_4$ ,  $0.1 \leq x \leq 1$ .
18. The battery of claim 16 wherein the lithium metal phosphate comprises  $LiFe_{1-x}Mn_xPO_4$ , where  $0.6 \leq x \leq 0.8$ .
19. The battery of claim 16 comprising an anode having lithium metal.
20. The battery of claim 16 comprising an anode having a lithium intercalation compound.

21. A collection of particles comprising a collection of amorphous particles, the particles comprising a phosphate composition having an average particle size less than about 95 nm and having essentially no particle with a diameter greater than about 5 times the average particle size.

22-47. (Canceled)

48. The collection of particles of claim 21 having a plurality of metals in the composition.

49. The collection of particle of claim 21 having at least three metals within the composition.

50. The collection of particles of claim 21 wherein the composition comprises lithium.

51. (Canceled)

52. The collection of particles of claim 21 having essentially no particle with an diameter greater than about 3 times the average particle size.

53. The collection of particles of claim 21 having a distribution of particle sizes such that at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

54. The collection of particles of claim 21 wherein the phosphate composition comprises  $\text{AlPO}_4$  or  $\text{Ca}_3(\text{PO}_4)_2$ .

55. A collection of particles comprising a crystalline composition with a phosphate anion and a lithium cation, the collection of particles having an average particle size less than about 1000 nm and having a distribution of particle sizes such that at least about 95

percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

56. The collection of particles of claim 55 having an average particle size from 5 nm to about 100 nm.

57. (Canceled)

58. A collection of particles comprising a collection of amorphous particles, the particles comprising a phosphate composition having an average particle size less than about 95 nm and having a distribution of particle sizes such that at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

59. The collection of particles of claim 58 having an average particle size from 5 nm to about 100 nm.

60. The collection of particles of claim 58 having a plurality of metals in the composition.

61. The collection of particle of claim 58 wherein the phosphate composition comprises  $\text{AlPO}_4$  or  $\text{Ca}_3(\text{PO}_4)_2$ .

## EVIDENCE APPENDIX

1. U.S. Patent 5,538,814 to Kamauchi et al.

## EVIDENCE APPENDIX

2. U.S. Patent 5,789,115 to Manev

## EVIDENCE APPENDIX

3. Striabel et al., "Comparison of  $\text{LiFePO}_4$  from Different Sources," Journal of the Electrochemical Society, **152**(4) A664-A670 (2005).



## Comparison of $\text{LiFePO}_4$ from Different Sources

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The lithium iron phosphate chemistry is plagued by poor conductivity and slow diffusion in the solid phase. To alleviate these problems, various research groups have adopted different strategies, including decreasing the particle sizes, increasing the carbon content, and adding dopants. In this study, we obtained  $\text{LiFePO}_4$  powders and/or electrodes from six different sources and used a combined model-experimental approach to compare the performance. Samples ranged from 0.4 to 15% "*in situ*" carbon. In addition, particle sizes varied by as much as an order of magnitude between samples. The study detailed in this manuscript allows us to provide insight into the relative importance of the conductivity of the samples compared to the particle size, the impact of having a distribution in particle sizes, and ideas for making materials to maximize the power capability of this chemistry.  
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Lithium iron phosphate ( $\text{LiFePO}_4$ ) is a promising candidate for low-cost lithium batteries because it has a high theoretical capacity (170 mAh/g), excellent stability during cycling, and prospects for a safer cell compared with  $\text{LiCoO}_2$ .<sup>1</sup> The major drawback with this material has been that it has low electronic conductivity, on the order of  $10^{-9}$  S/cm.<sup>2</sup> This renders it difficult to prepare cathodes capable of operating at high rates. Significant research has recently been focused on the incorporation of conductive carbon into the active material powders<sup>3-5</sup> or the doping of the  $\text{LiFePO}_4$  structure to improve its electronic conductivity.<sup>2,6</sup> Our group has been studying the carbon-coated  $\text{LiFePO}_4$  invented at Hydro-Quebec<sup>3</sup> and now supplied by PhosTech (Montreal, Canada) in pouch cells prepared with natural graphite anodes and either liquid<sup>7</sup> or gel electrolytes.<sup>8</sup> Huang *et al.* reported the preparation of  $\text{LiFePO}_4$  in a carbon gel matrix where the active material is dispersed in a carbon prepared from a resorcinol gel.<sup>4</sup> More recently, other labs are reporting excellent results from carbon-coated  $\text{LiFePO}_4$  made by other techniques such as gel-coating<sup>9</sup> and a carbothermal technique.<sup>10</sup> In addition to having low electronic conductivity, lithium and/or electron diffusion in the active material has been reported to be slow, with considerable loss in utilization with increasing current.<sup>11</sup>

Because of the low electronic conductivity of the active material,  $\text{LiFePO}_4$ , the performance of a  $\text{LiFePO}_4$  cathode depends on the amount of carbon in the structure, either *in situ* (i.e., either formed during the preparation of the active material or formed intentionally by adding, e.g., sugar solution followed by carbonization) or mixed in with the binder. However, Doeff *et al.* also found that the relative quality of the *in situ* carbon on the  $\text{LiFePO}_4$  particles plays a major role in cathode performance.<sup>12</sup> The quality of the carbon, resulting from the addition of different organic precursors, was compared by measuring the  $\text{sp}^2/\text{sp}^3$  character of the carbon in the  $\text{LiFePO}_4$  after firing, by Raman spectroscopy.

In another approach to the problem, Chiang *et al.* claimed that doping (substituting) of part of the Li in the structure for Nb, Zr, or Mg resulted in an increase in the electronic conductivities by eight orders of magnitude.<sup>2</sup> However, there have recently been some challenges to those findings.<sup>13</sup> The improvement of the electronic conductivity of an active-material powder is difficult to measure because most preparations involve organic precursors that result in residual carbon. In addition, the conductivity measurement requires dense pellets that, in turn, require higher temperatures (for sintering) than what is used to prepare cathode-active powders. This increases the risk for converting part of the  $\text{LiFePO}_4$  into other (highly conductive) phases such as  $\text{Fe}_2\text{P}$ .<sup>14</sup>

There are clearly several approaches to the preparation of a low

electronic conductivity active material, such as  $\text{LiFePO}_4$ , into a high-performance cathode. The relative intrinsic conductivity as well as the location and quality of the added or *in situ* carbon play a role. In addition, poor solid-phase transport means that the utilization of the active material is a strong function of the particle size. Together, these factors lead to a strong dependence of cathode performance on the loading and thickness of the electrode. This dependence on loading makes it difficult to compare the merits of different preparation techniques for  $\text{LiFePO}_4$ . In this work, we prepared cathodes from many sources of  $\text{LiFePO}_4$ . The performance at different rates was measured in half-cells, and the inevitable differences in cathode design were normalized through the use of a mathematical model of the discharge process in the  $\text{LiFePO}_4$  cathode.

The model is based on the one developed previously by Doyle *et al.* in that it incorporates charge and mass balance in the porous electrode and reaction at the interface.<sup>15</sup> Whereas the previous models have described the solid-phase phenomenon using intercalation behavior (diffusion in spherical coordinates), the present model describes the phase change that is known to occur in  $\text{LiFePO}_4$  using the "shrinking core" approach<sup>16</sup> in keeping with X-ray diffraction (XRD) evidence of the existence of two phases.<sup>11</sup>

### Experimental

$\text{LiFePO}_4$  powders with varying amounts of *in situ* carbon (carbon resulting from the phosphate preparation) were used as received from the Institute of Chemistry (Ljubljana, Slovenia), Hydro-Quebec (HQ) (Quebec, Canada), the University of Waterloo (Waterloo, Canada), and the State University of New York (SUNY, Binghamton, NY). The  $\text{LiFePO}_4$  powders were combined with carbon black (Shawinigan) and/or graphite (SFG-6) and mixed into a slurry with poly(vinylidene fluoride) (PVdF, Kureha)/N-methyl pyrrolidone. Slurries were cast with a knife-edge coater on carbon-coated Al current collectors, prepared in-house from a very thin coating of PVdF-bonded Shawinigan black. These electrodes were made in a near-identical manner to minimize the impact of electrode construction. In addition, premade cathodes were received from the Massachusetts Institute of Technology (MIT) and the Lawrence Berkeley National Laboratory (LBNL) Materials Science Division. The MIT cathode was prepared from 1% Zr-doped  $\text{LiFePO}_4$ ,<sup>2</sup> and the LBNL cathode contained  $\text{LiFePO}_4$  prepared with the sol-gel technique with the addition of pyromellitic acid to the precursor mix.<sup>12</sup> The compositions of each electrode (i.e., active material, carbon and/or graphite and binder content) as well as thickness and loading were known. Several of these parameters are listed in Table I. The electrodes were tested in identical Swagelok cells with the same electrode area (1 cm<sup>2</sup>) and a spring-loaded current collection piston so as to maintain similar compression during testing. However, as the two premade cathodes were not constructed in an identical manner to the rest, changing the fabrication technique could yield differences in the results from the ones reported in this paper. In other words, the

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Table 1. Properties of LiFePO<sub>4</sub> powders and cathodes.

Source	<i>In situ</i> carbon (%)	Particle size (nm)	Crystallite size (nm)	Active loading (mg/cm <sup>2</sup> )	Total carbon (%)	Binder (PVdF) (%)	Electrode thickness (μm)	C/25 capacity (mAh/g)
Low-carbon	0.40	NK <sup>a</sup>	43	10.4	9	10	90	91
LBNL	0.9	700	200	7.3	12.7	8	70	149
MIT	<1	50-100	36	4.4	10	11	55	150
HQ	1-2	200	77	9.2	9	10	85	144
Slovenia	6.1	<100	30	8.9	10	10	85	144
Waterloo	15	100-200	81	7.8	17.2	8	80	130

<sup>a</sup> NK Not known.

model parameters extracted for these two cathodes would be a reflection of not only the materials characteristics, but also the electrode-construction characteristics. However, the LBNL cathode construction recipe is similar to the ones used in this paper; therefore, the impact of electrode construction is expected to be minimal on the results reported here.

The powders were analyzed with XRD to verify phase purity and get an estimate of the average crystallite size by whole pattern fitting. Cathode performance was tested in a half-cell, as discussed above, containing Li reference and counter electrodes, with either 1 M LiPF<sub>6</sub> or 1 M LiBF<sub>4</sub> in ethylene carbonate/diethyl carbonate electrolyte and Celgard separators. Electrode capacity was determined at a low rate (~C/25), and high-rate utilization was measured at discharge rates from C/5 to 10C (based on a capacity of 170 mAh/g), as controlled with an Arbin Battery Cycler (College Station, TX).

### Model Development

The model developed describes the diffusion of lithium and/or electrons in the solid phase and the phase change in the material using the shrinking-core approach, with a core of one phase covering a shell of the other phase, as described previously.<sup>16</sup> The model solves for the diffusion in the shell and the movement of the phase interface by assuming that the concentration at the phase interface is at equilibrium. In addition, the distributed reaction in the porous electrode is described using porous electrode theory, and the change in concentration of the electrolyte is accounted for using concentrated solution theory, as described previously.<sup>15</sup> Two particle sizes are included in the model to approximate the behavior of a true particle size distribution. The carbon coating that is known to exist in this material is not described in the model, and no distinction is made between this carbon and the extra added carbon when electrodes are fabricated. Instead, all conductivity effects are combined into the matrix phase conductivity, whose magnitude is thought to capture the impact of both these carbons.

Note that in the solid iron-phosphate particles, the lithium and the electron are envisioned to form a dilute binary electrolyte. This allows us to collapse the diffusion and migration terms into a single Fick's law-type equation, as shown in Newman.<sup>17</sup> This means that the diffusion coefficient used in this paper is an effective diffusion coefficient which takes the form

$$D = \frac{z_+ u_+ D_- - z_- u_- D_+}{z_+ u_+ - z_- u_-} \quad [1]$$

where  $z$  represents the charge on the ion,  $u$  the mobility, and  $D$  the diffusion coefficient. The subscript  $+$  represents the Li ion and the  $-$  represents the electron. Using the Nernst-Einstein relationship to relate the mobility to the diffusion coefficient and substituting in the charge of the electron and the lithium ion, Eq. 1 can be rewritten as

$$D = \frac{2D_+D_-}{D_+ + D_-} \quad [2]$$

Therefore, the diffusion coefficient used in this paper depends on the relative magnitude of the electron and lithium-ion diffusion coefficients. Recently, Morgan *et al.* used first-principle calculations to estimate the diffusion coefficient of lithium in LiFePO<sub>4</sub> assuming that the concentration and mobility of electrons are large.<sup>18</sup> The authors concluded that the transport of lithium in the lattice is very large (of the order of  $10^{-9}$  cm<sup>2</sup>/s), thereby suggesting that electron transport is slower than lithium-ion transport in this material.<sup>18</sup> Using this result in Eq. 2 suggests that the diffusion coefficient used in this paper ( $8 \times 10^{-18}$  m<sup>2</sup>/s) would be two times the diffusion coefficient of electrons in the LiFePO<sub>4</sub> lattice. However, if lithium transport is also equally important when compared to the electron transport, as argued by Yang *et al.*,<sup>19</sup> then, using this result in Eq. 2 suggests that the diffusion coefficient used here is equal to the diffusion coefficient of lithium ions (which is similar to that of the electrons).

We have previously used a well-characterized cell, based on the HQ material, where the particle sizes, area for reaction, loading, and thicknesses were known, to compare the model to the data and extract unknown parameters.<sup>16</sup> This cell was used to estimate the equilibrium potential expression and the composition ranges of the single-phase regions in the material. The diffusion coefficient of electrons in the material was fit using the model to experimental data, resulting in a value of  $8 \times 10^{-18}$  m<sup>2</sup>/s, consistent with values reported in the literature. The kinetics was assumed to be large, keeping with the prevalent view that the Li reaction is facile. A value of  $3.14 \times 10^{-6}$  A/m<sup>2</sup> [at a reference concentration of 1 M and 50% state of charge (SOC)] was used for the simulations. These two values were then maintained for all the simulations reported here. All electrolyte properties were the same as those used in Ref. 16 and correspond to LiPF<sub>6</sub> salt in either ethylene carbonate (EC):ethylmethyl carbonate or EC:diethyl carbonate. One cathode used in this study (MIT) was cycled in LiBF<sub>4</sub> electrolyte, but due to lack of transport properties for this salt, the simulations were conducted using the properties for LiPF<sub>6</sub>. We have previously shown<sup>16</sup> that electrolyte drops are negligible in cells with thickness and porosities similar to those used in this study. Hence, the electrolyte transport properties used should have little impact on the results presented here.

The comparison of the various materials reported here was performed by first fitting the model to experimental data at various rates to extract the two particle sizes, the matrix conductivity, and the contact resistance, and then using these numbers to simulate behavior for a fixed cell design. Measuring particle sizes using transmission electron microscopy (TEM) can be difficult due to agglomeration effects. In addition, the technique results in a range of sizes, whereas the model requires the use of two characteristic sizes which give the same overall behavior as the real electrode. Finally, the

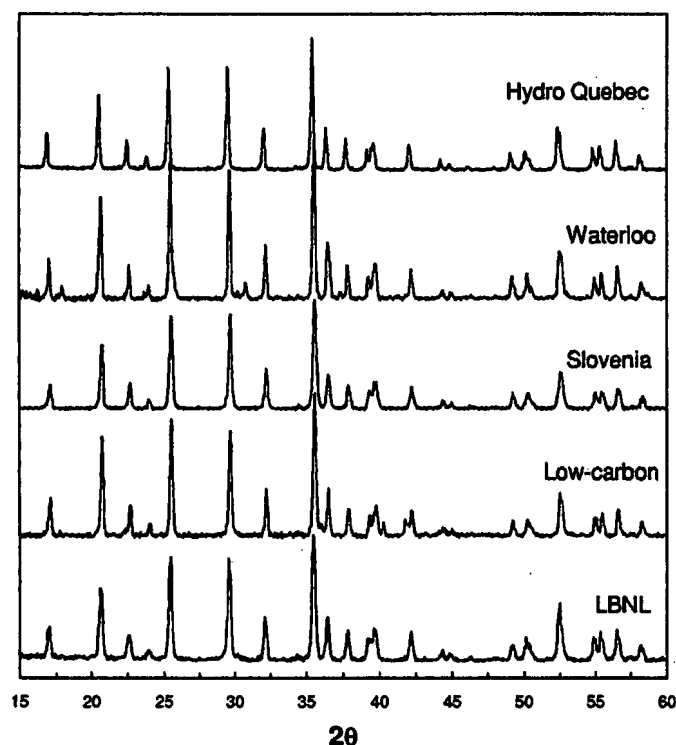


Figure 1. XRD diffraction pattern for five of the  $\text{LiFePO}_4$  samples used in this study.

surface area measurements based on the Brunauer, Emmett, and Teller method from which particle size can be estimated, can result in areas that can be different from the electrochemical surface area, especially for samples that have a lot of carbon. For these reasons, the particle size was chosen as a fitting parameter. The approach used for incorporating the particle size involves three additional parameters: the sizes of the small, the large, and the average particles. The sizes of the small and large particles dictate the transport losses in the system, and the size of the average particle is needed to find the total surface area of reaction, which in turn affects the kinetic losses. As the exchange current density is taken to be fairly large, the area has little impact on the simulations; therefore, the model can be thought to have two unknown parameters that describe the particle size. We first fit the model to the utilization at the largest current to find the size of the small particle. Subsequently, we fit the utilization at the lowest current to find the size of the large particles. The parameters are then tested by predicting the utilization at other currents. An average value between these two limits was used for the area calculations. As noted earlier, this quantity has little significance to the results shown in the paper. The slope of the potential-capacity curve at intermediate capacity values at the largest current is then used to extract the matrix-phase conductivity. This slope occurs because of a changing reaction distribution in the porous electrode as discharge proceeds. Subsequently, we fit the voltage drop at this current to find the contact resistance between the current collector and the electrode. The contact resistance was negligible for all materials except for the one prepared by the MIT group. These two values are then tested by predicting the voltage and the slope at all other currents. For each material, the C/25 discharge curve was assumed to represent the equilibrium potential in the single-phase region and a curve fit to an equation was used in the model. This data was also used to calculate the maximum capacity of each electrode. Once these parameters are extracted and tested, the comparison of the various materials is performed by simulating their behavior for a single thickness, porosity, and volume fraction of active material.

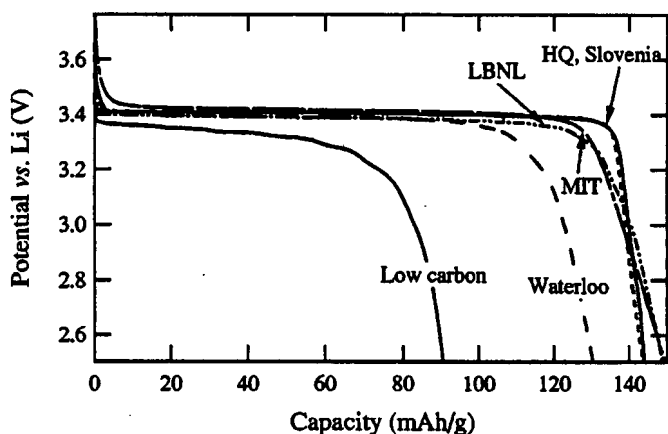


Figure 2. Slow rate (C/25) discharge curves of the six  $\text{LiFePO}_4$  electrodes vs. Li reference and counter electrodes measured at 25°C.

## Results and Discussion

**$\text{LiFePO}_4$  materials properties.**—The samples were received over a period of a year and do not necessarily represent the best  $\text{LiFePO}_4$  from any of the labs. The low-carbon sample from SUNY was included as a baseline material to show the performance of  $\text{LiFePO}_4$  with very low carbon content. However, the carbon in this sample was measured to be 0.4% by Luvak Laboratories (Boylston, MA). This amount of carbon resulted from the incomplete combustion of the organic precursors. XRD analysis was carried out for

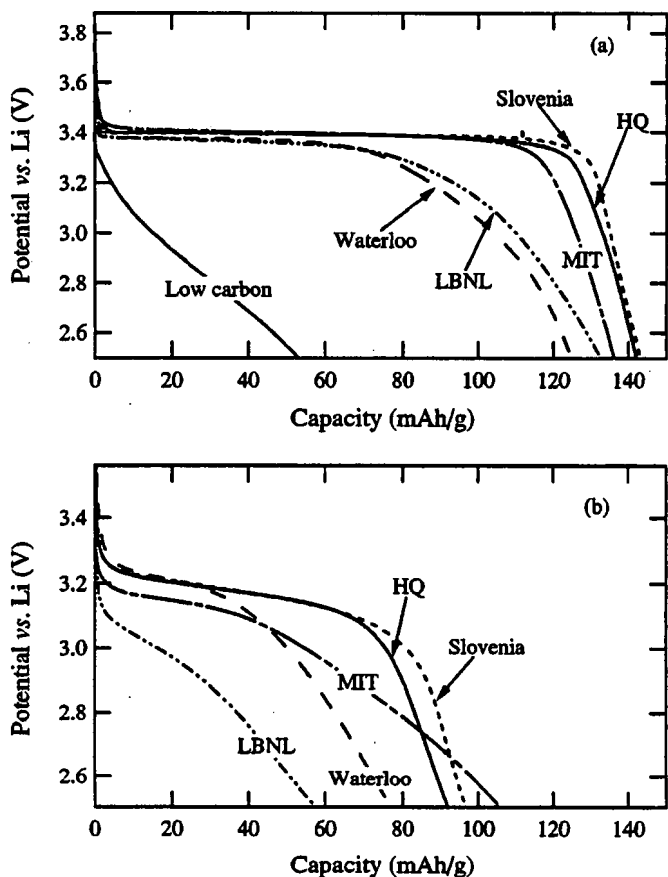


Figure 3. Experimental discharge curves at (a) C/5 and (b) 5C rates for six  $\text{LiFePO}_4$  electrodes. At 5C the sample with low-carbon coating is not shown as there was no useful capacity in the material.

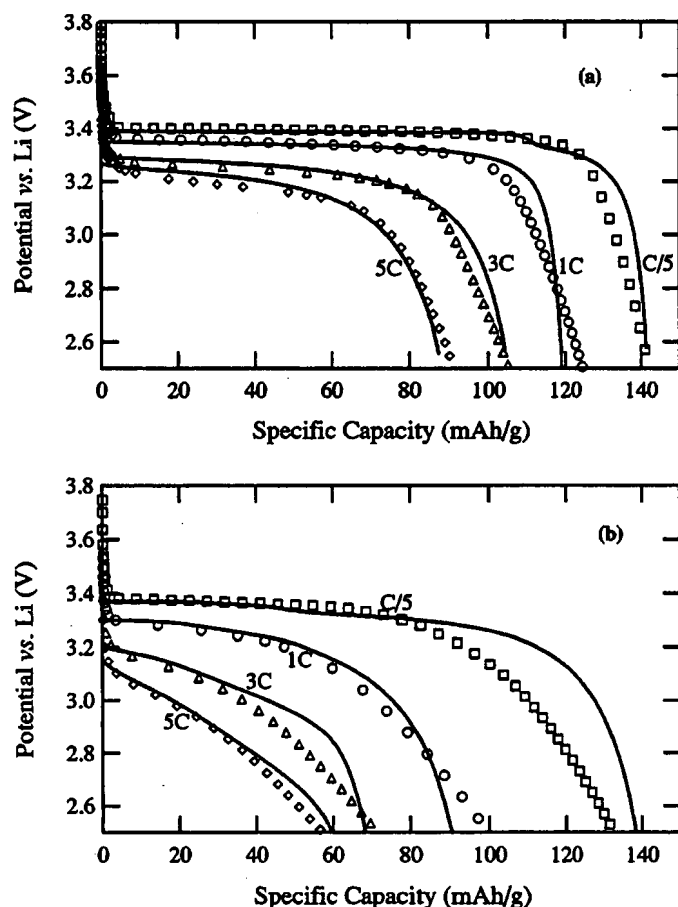


Figure 4. Model-experimental comparisons of discharge curves at various rates for (a) HQ and (b) LBNL material. See text for details.

most of the electrodes, as shown in Fig. 1. Comparison of the powder pattern for all  $\text{LiFePO}_4$  samples shows that they are well crystallized in the orthorhombic ( $Pmn2_1$ ) structure of  $\text{LiFePO}_4$ .<sup>20,21</sup> However, some powders show a few very weak reflections from  $\text{Fe}^{3+}$ -containing impurities such as iron oxide and/or lithiated iron oxide. The weak reflections are mostly due to the low concentration of material in the powders as well as the lower crystallinity. Crystallite sizes were calculated from these diffraction data by whole-pattern fitting. These are summarized in Table I, along with the sources of  $\text{LiFePO}_4$ , the percentage of *in situ* carbon (carbon resulting from the preparation process), and estimates of the primary particle sizes taken from the literature or supplied by the various sources of the  $\text{LiFePO}_4$  materials. The large variety in particle sizes and particle-size distributions mirrors the wide variety in preparation techniques used for the active materials.

**Electrochemical studies.**—The compositions and loadings for the different cathodes tested are listed in Table I. The fraction of active material in the cathode matrix fell in the range of 75–82%. It was not possible to keep the total carbon content the same because the Waterloo active-material powder contained 15% carbon and the MIT cathode only 10%, as received. All the cathodes were tested with two cycles at C/25. The second of these discharge cycles is compared in Fig. 2. A specific capacity close to 150 mAh/g was observed for all of the cathodes except for the highest and lowest *in situ* carbon samples (0.4 and 15%), as summarized in Table I. The capacity of the Waterloo material was much lower than reported previously<sup>4</sup> and may hint at a degradation process in this material. Note the differences in the shape of the equilibrium curve at the end of discharge. Whereas the drop in potential is very sharp for the materials prepared by HQ and Slovenia, the other samples show a

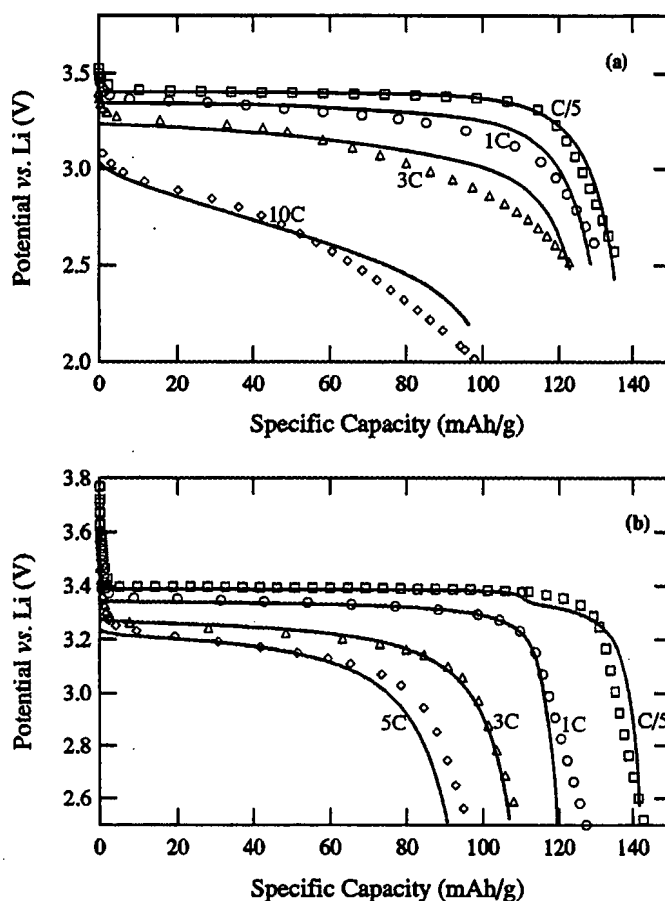


Figure 5. Model-experimental comparisons of discharge curves for (a) MIT and (b) Slovenia material. See text for details.

more gradual drop. Although a C/25 discharge may not be a true thermodynamic measurement, this may indicate differences in the phase composition in these materials.

Our standard protocol for variable-rate measurements uses a constant charge at C/2, so that all the discharges start from the same place and the test can finish in a timely fashion. However, for modeling purposes, it is more convenient to assume that the cathode starts at a fully charged state before each variable-rate discharge. Therefore, except for the MIT cathode, the variable-rate discharge data used for the modeling effort were recorded after a C/25 charge. The curves for the C/5 and 5C discharges for the six  $\text{LiFePO}_4$  cathodes are compared in Fig. 3a and 3b, respectively. Clearly, some treatment of the  $\text{LiFePO}_4$ , either doping or deliberate *in situ* carbon, is necessary for adequate performance of  $\text{LiFePO}_4$ . This is consistent with the early work with uncoated samples.<sup>11</sup> However, further comparison of these data is difficult, because the best discharge curve (for the MIT cathode) is also for the lowest-loading cathode. For this reason, these data were used for fitting purposes to enable comparisons between electrodes with the same design.

**Model fits and predictions.**—The model described previously was run for all six sets of cathode discharge data, and the results are presented in Fig. 4–6. Figure 4a shows the model-experimental comparisons for the HQ material. The excellent fits seen in this case are expected considering that this is the baseline used to extract the unknown parameters. The model does not predict the initial sharp drop in potential before the plateau region. We believe that this is caused by a narrow single-phase region in the completely delithiated material. As this single-phase region is not included in the model, no prediction of this behavior is expected. The knee in the low-rate (C/5) curve in Fig. 4a is caused by the two particle sizes in the

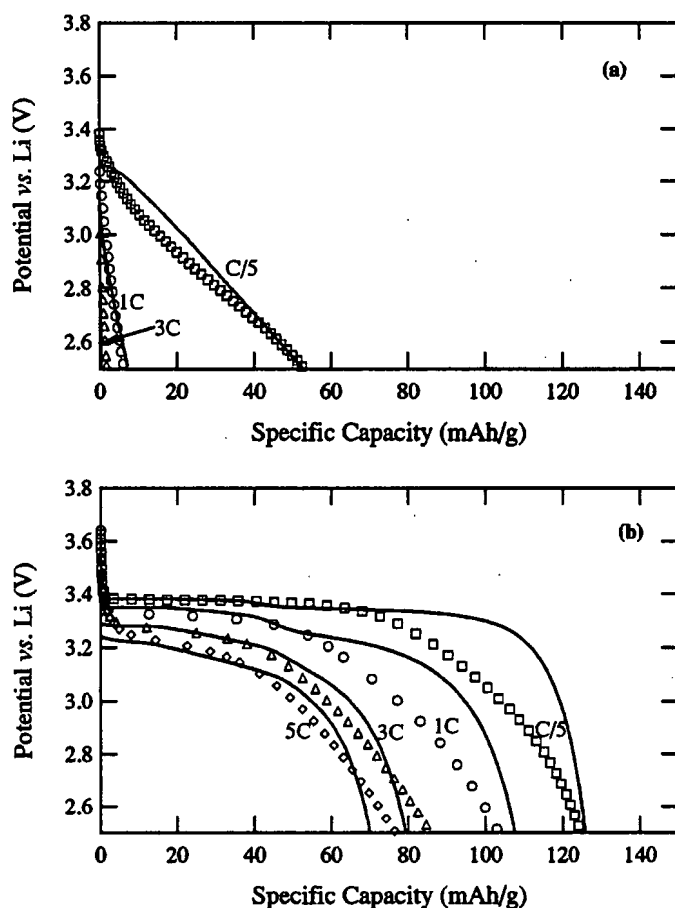


Figure 6. Model-experimental comparisons of discharge curves for (a) low carbon and (b) University of Waterloo material. See text for details.

model. As discharge proceeds, the small particles fill up faster than the larger ones. Typically, this mismatch in the SOC can be expected to result in a greater change in the equilibrium potential of the small particles compared to the large, resulting in a larger overpotential, thereby allowing the larger particles to "catch up." However, the relatively flat potential for this two-phase system does not allow this to occur, and the mismatch between the two particles increases until the small particles are almost completely filled. At this point, the potential drops, and the reaction shifts to the larger particles, resulting in a second plateau. Clearly, incorporating more particle sizes into the model would remove this artifact.

The model predictions for the LBNL material (Fig. 4b) are also excellent, especially in predicting the voltage drops with current. The fit is lacking in predicting the final drop in potential, especially at low rates. The particle sizes extracted for this material had one of

the largest ranges among all the materials studied here (see Table II). This suggests that the model needs to incorporate more particle sizes to predict this final decrease in voltage accurately.

Figure 5a shows the predictions for the material from MIT. As mentioned, this material shows a significantly sloped profile at the end of discharge at low rates as compared to the other materials studied. The remarkable utilization of this material is clear in the figure, where the discharge at the 3C rate shows a potential profile that suggests that decreasing the potential cutoff below 2.5 V would have resulted in the material being completely utilized. This material stands out as having the best high-rate utilization. However, as the rate increases, potential drops occur in this material, suggesting that the preparation conditions have not resulted in an optimum matrix conductivity. In addition, this was the only electrode where a contact resistance was needed to get adequate fits to the data. A value of  $0.0017 \Omega\text{-m}^2$  fit the data adequately.

Figure 5b shows the comparison for the Slovenia material. Both the behavior of the material and the extracted parameters are comparable to those from the HQ material. Finally, Figure 6a shows the predictions of the material without carbon and Fig. 6b those of the material from the University of Waterloo. The poor utilization of the material without carbon, even at relatively low rates, is due to the voltage reaching the cutoff potential much before any transport limitations become important. As the electrode is ohmically limited, extracting transport-related quantities (particle size) is not possible. The University of Waterloo material shows excellent prediction of the voltage with current, but poor fits in the drop in voltage at the end of discharge, similar to the material from LBNL (Fig. 4b). This material has an even larger size difference between the small and large particles, as predicted by the model. These two materials (Waterloo and LBNL) show a much larger range when compared to the other materials tested here, and this large range correlates with the inability of the model to predict the voltage drops at the end of discharge at low currents. This qualitative correlation gives credence to the assertion that incorporating more particles would give better fits in this region.

Table II summarizes the particles sizes and matrix conductivities extracted using the model for all the materials. Note that this is an indication of the smallest length scale over which diffusion occurs and is therefore different from an agglomerate size, typically reported in the literature. The sizes extracted are of the order of the crystallite size for the various materials (Table II). In some cases (e.g., LBNL), the small particle size extracted is smaller than the crystallite size. This is a consequence of using two sizes to approximate a true distribution. It is clear that the MIT cathode data were fit with the smallest size and smallest range of particle sizes. We believe that this feature is the cause for the excellent behavior of the MIT material. The agreement with their particle-size data (from TEM) is remarkable. The particle sizes for the low-carbon sample are not significant due to the fact that the electrode was so ohmically limited. The fits of the HQ and the Slovenia cathodes were similar, although that for the HQ gave significantly higher matrix conduc-

Table II. Model fits and comparisons.

Source/name	Crystallite size (nm)	Amount of carbon		Parameters from model fit		
		Total (%)	<i>In situ</i> (%)	Matrix cond. (S/m)	Particle size (nm)	
					Small	Large
HQ	77	9	1-2	50	61	144
Slovenia	30	10	6.1	0.1	58	137
Waterloo	81	17.2	15	0.03	21	340
LBNL	200	12.7	0.9	0.01	62	608
MIT	36	10	<1	0.01	64	119
Low carbon	43	9	0.4	0.00035	133	288

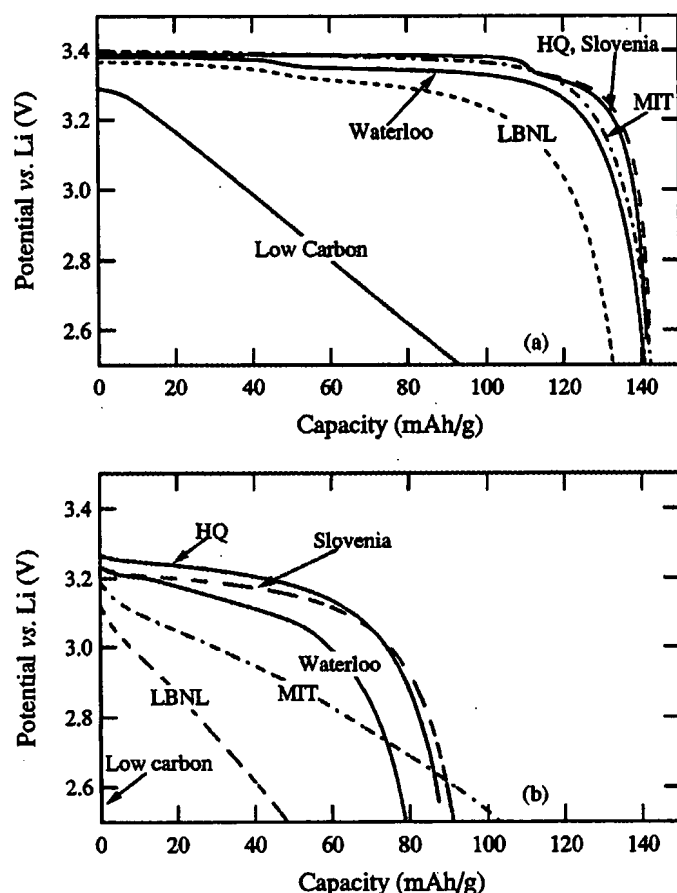


Figure 7. Simulated discharge curves for the six materials used in this study at (a) C/5 and (b) 5C rates. Compare with Fig. 3, which shows results for different designs. Fig. 7 results are for the same design.

tivity. Note that the matrix conductivity value for the HQ electrodes is large enough that ohmic drops are minimal.

The fitting parameters from each source of  $\text{LiFePO}_4$  were used to calculate the expected performance for a cathode  $85\text{ }\mu\text{m}$  thick and with an active material loading of  $9.175\text{ mg/cm}^2$  (the same as the HQ electrode). The calculated C/5 and 5C curves are shown in Fig. 7 and can be compared to the experimental results in Fig. 3. Whereas Fig. 3 shows the experimental data with a different cell design for each material, Fig. 7 shows the simulations for the same cell design. Note that the Waterloo material has almost ca.  $140\text{ mAh/g}$  in Fig. 7a as the mass of all the materials has been made the same to provide a fair basis for the comparison. In addition, to make the comparison of the MIT material fair, no contact resistance was used in these simulations. The excellent utilization of this material is clearly seen in Fig. 7b, although the potential drops are more significant.

The impact of the decreasing utilization and the drop in potential with current can be captured in one plot by estimating the energy of the cell (area under the voltage-capacity curve) and plotting it against the average power (energy divided by the time of discharge), in the form of a Ragone plot, as shown in Fig. 8. As expected, the electrode with the lowest *in situ* carbon shows the worst performance, while the electrodes from HQ and Slovenia show the best high-rate capability. Although the MIT material shows much better intermediate-rate behavior, a consequence of its smaller particle size, at higher rates, ohmic drops become more important and the energy decreases. The two materials that have the widest particle size range, LBNL and Waterloo, show poor intermediate-rate capability. Of these two, the Waterloo material performs better due to the material's lower average particle size.

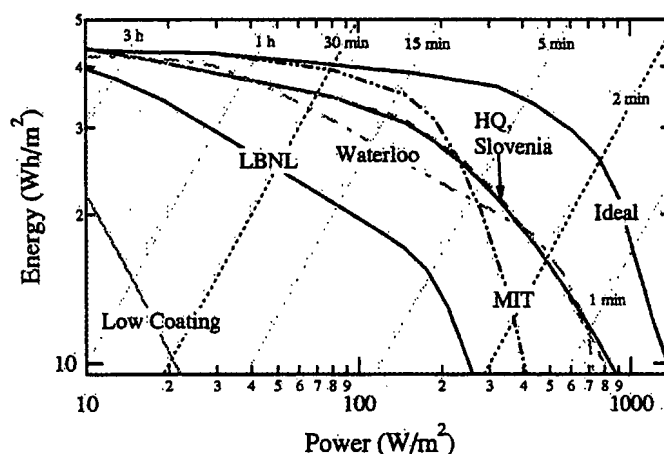


Figure 8. Simulated Ragone plot for the materials studied here. Curves were generated using the parameters extracted from the model-experimental fits, as described in the text, and using these values for a constant cell design. Curve marked Ideal represents a hypothetical cell with particle sizes taken from the MIT material and conductivity of the matrix taken from the HQ material.

**Ideal case.**—To give the reader an estimate of what can be achieved for this material, we performed a hypothetical simulation by using the best features of these different materials and represent it by the line marked Ideal in Fig. 8. This line was generated by using the particle size of the MIT material and the conductivity of the HQ material. Clearly as much as a doubling of the power capability can be achieved by better material preparation techniques. Each of the materials shown in the figure can be made to achieve this ideal performance, but changes would need to be made to the material properties. In summary, Fig. 8 suggests that for this chemistry to be made more competitive three strategies should be pursued: (i) the particle size should be made smaller, (ii) the particle size ranges should be minimized, and (iii) the matrix conductivity should be improved. Figure 8 also suggests that all three factors are equally important.

However, decreasing the particle size can lead to electrode fabrication issues and could lower the volumetric energy density, caused by the decreasing tap density, as suggested by Chen and Dahn.<sup>22</sup> In addition, smaller particles would require more carbon and binder to bind the particles together to form an electrode, thereby resulting in decreased specific energy. This aspect is beyond the scope of this study; hence, no conclusions can be drawn on an optimum particle size to be used in these electrodes.

## Conclusions

Six  $\text{LiFePO}_4$  electrodes having different particle sizes, carbon contents, porosities, and thickness were examined in this study to understand the mechanism that improves the power capability of this chemistry. This insight is provided by combining experimental data at various rates with a mathematical model. The study suggests that carbon coating is critical as it provides the electron with a more conductive path, thereby decreasing ohmic drops. Although the amount of carbon coating seems immaterial as long as a coating is achieved, the quality of the carbon is important. However, the coating can be eliminated if the active material can be made more conductive, e.g., via doping. However, carbon is still needed to carry the electron from the current collector to the reaction site; therefore, electrode construction can have a significant impact on performance. Finally, the utilization of the material can be poor if the particle size is large, or if the distribution of particle size is wide.

## Acknowledgments

We gratefully acknowledge the supply of cathode powders and electrodes from Hydro Quebec, the University of Montreal, MIT, the

University of Waterloo, and the State University of New York at Binghamton. We thank T. Richardson and S. W. Song for the XRD measurements. This research was funded by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Freedom-CAR, and Vehicle Technologies of the U.S. Department of Energy under contract no. DE-AC03-76SF00098.

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## EVIDENCE APPENDIX

### 4. 132 Declaration and Attachments



PATENT APPLICATION  
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Attorney Docket No.: 2950.20US01

Chaloner-Gill et al.

Confirmation No.: 2942

Application No.: 09/845,985

Examiner: Mark Ruthkosky

Filed: April 30, 2001

Group Art Unit: 1745

For: PHOSPHATE POWDER COMPOSITIONS AND METHODS FOR FORMING PARTICLES  
WITH COMPLEX ANIONS

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DECLARATION UNDER 37 C.F.R. § 1.132

Mail Stop Amendments  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

We, Craig R. Horne, Ph.D. and On K. Chang, Ph.D., hereby declare as follows:

1. Craig R. Horne, Ph.D. is presently Director, Electrochemical Applications at NanoGram, Corp. Dr. Horne was awarded his Ph.D. in Materials Science & Mineral Engineering from the University of California, Berkeley in 2000. Dr. Horne has eight published technical papers, has been active in the Electrochemical Society and has referred papers for the Journal of the Electrochemical Society. Dr. Horne has been an employee or consultant to NanoGram, its parent company NeoPhotonics or its majority owned subsidiary Kainos Energy Corporation since he departed Berkeley in 1998. Dr. Horne is an inventor on 10 issued U.S. Patents and numerous U.S. and foreign pending applications. More details on Dr. Horne's qualifications are found on the attached resume.
2. On K. Chang, Ph.D., is presently a consultant for NanoGram Corp. Dr. Chang received his Ph.D. from the University of California, Davis in Physical Chemistry in 1985. Dr. Chang has nine scientific publications and has worked extensively in the battery and battery materials area



from 1986 to the present. In particular, except for two years working on semiconductor packaging, Dr. Chang has worked in the battery areas for this entire time. Dr. Chang is an inventor on 20 issued U.S. Patents. More details on Dr. Chang's qualifications are found on the attached resume.

3. Dr. Horne is an inventor on the patent application noted above that is presently under examination. Dr. Chang is not an inventor on this patent application. However, he has reviewed the pending claims in this application.

4. We have carefully read U.S. Patent 5,538,814 to Kamauchi et al. (the Kamauchi patent). We have reproduced the formation of lithium cobalt phosphate based on the teachings of the Kamauchi patent. Specifically, we followed a procedure similar to the procedure of Example 1 of the Kamauchi patent. Thus, we mixed lithium carbonate, cobalt carbonate hydrate and 85% phosphoric acid to achieve an atomic ratio of  $\text{Li}:\text{Co}:\text{P} = 2:1:1$ . We used cobalt carbonate hydrate as a substitute for basic cobalt carbonate, which generally has cobalt hydroxide as a contaminant, due to its higher purity. As noted in the Example, this results in a mixed phase material comprising lithium phosphate, lithium-cobalt phosphate and cobalt oxide. As described in the Kamauchi patent, the reaction mixture was heated at  $900^{\circ}\text{C}$  for 24 hours. Further details are in the attached report.

5. In addition to the formation of lithium cobalt phosphate, we also synthesized lithium iron phosphate using techniques similar to known approaches and the approach in the Kamauchi patent. Specifically, the  $\text{LiFePO}_4$  was synthesized using the procedure in the Kamauchi patent with some revisions based on a procedure published in an article by A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, "Phospho-olivines as Positive Electrode Materials for Rechargeable Lithium Batteries," *J. Electrochemical Society*, 144(4): 1188-1193 (1997). Our synthesis reaction involved Fe(II) oxide, 85% phosphoric acid and lithium carbonate. Iron (II) carbonate, corresponding to the cobalt carbonate of the Kamauchi process, is not commercially available and is thought to be unstable due to spontaneous decomposition to iron oxide and carbon dioxide. Also, iron (II) oxide is known to react with phosphoric acid to form iron phosphate so it seemed to be an appropriate reactant. Phosphoric acid was used since it was used

in the Kamauchi patent. Relative to the Padhi et al. process, we substituted Fe(II) oxide for Fe(II) acetate and 85% phosphoric acid for ammonium phosphate. In our synthesis reaction, an initial heating step was performed at 300 to 350°C, which was followed by heating at 800°C for 24 hours. The heating was done in a nitrogen environment, as taught in Padhi et al. since it is thought that heating in the presence of oxygen would form Fe(III). The resulting composition was confirmed with an x-ray diffractogram so that the substitutions did not change the product composition. Further details are in the attached report.


6. The as synthesized phosphate powders were processed using ball milling. The Kamauchi patent does not describe their milling techniques in detail. However, Example 7 at column 18 describes ball milling as a suitable milling approach. Similarly, Example 10 describes milling in a ball mill for 24 hours. This is the approach that we adopted for processing of the phosphate powders. A commercial ball mill was used, and the powders were milled for 24 hours. The results of our phosphate particle processing is described in detail in the attaches report entitled "Grinding of Lithium Cobalt Phosphate Mixed Phase Material (Li-Co-PO<sub>4</sub>) and Lithium Iron Phosphate (LiFePO<sub>4</sub>)." The results of which are summarized in the following.

7. The ground phosphate powders were evaluated using both visual evaluation of scanning electron micrographs (SEM) and light scattering of powders dispersed in a liquid. Transmission electron micrographs were not obtained since these would not have been meaningful beyond the SEM photos due to the large particles in the samples and the large range of particle sizes. The non-uniformity of the powders is readily observable in the SEM photographs, which clearly show tiny particles as well as relatively large chunks. These results are consistent with the light scattering results, which clearly show a very broad distribution of particle sizes. Plots in the attached report show the particle size distribution by volume as well as by particle number for the two phosphate samples. The light scattering results were performed with an ultrasonic probe to break agglomerates. This state of the art dispersion approach should be very effective at separating particles within agglomerates. The light scattering measurements were performed by an independent contractor based on samples that we provided.

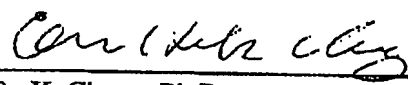
8. These particle size measurements clearly demonstrate that conventional grinding approaches cannot produce phosphate powders with close to the uniformity of the phosphate powders claimed in the pending claims of the present application.

9. We each independently declare that all statements made herein that are of my own knowledge are true and that all statements that are made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Apr 5 2006  
Date

  
Craig R. Horne, Ph.D.

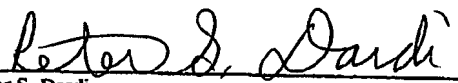
Apr. 5, 2006  
Date

  
On K. Chang, Ph.D.

CERTIFICATE OF FACSIMILE TRANSMISSION

I hereby certify that this paper is being transmitted by facsimile to the U.S. Patent and Trademark Office, Fax No. 571-273-8300 on the date shown below thereby constituting filing of same.

April 6, 2006  
Date

  
Peter S. Dardi

# **Grinding of Lithium Cobalt Phosphate Mixed Phase Material (Li-Co-PO<sub>4</sub>) and Lithium Iron Phosphate (LiFePO<sub>4</sub>)**

On Chang and Craig Horne

NanoGram Corporation

## **BACKGROUND**

The purpose of this experiment is to evaluate the particle size distribution of metal phosphate nanoscale particles produced by following the teaching of U.S. Patent 5,538,814, the Kamauchi patent. For completeness, this demonstration was performed on two separate metal phosphate systems: (a) the Li-Co-PO<sub>4</sub> mixed-phase material that is the specific example in the Kamauchi patent, and (b) LiFePO<sub>4</sub>.

## **EXPERIMENTAL**

### **Chemicals**

Cobalt (II) carbonate hydrated: Sigma-Aldrich, Cat. No. 202193, Lot No. 05130JC  
Lithium carbonate: Sigma-Aldrich, Cat. No. 255823, 99% ACS grade, Lot No. 08004KC  
Phosphoric acid: Ashland chemical, 85%, semiconductor grade  
Iron (II) Oxide: Sigma-Aldrich, Cat. No. 400866, 99.9%, Lot No. 13722PC

### **Equipment**

Jar mill: One-tier jar high-capacity laboratory jar mill, 13" roller, Cole Parmer, Cat. No. EW-04149-00  
Milling jar: HDPE milling jar, 0.25 gal, with ridges on the interior to improve tumbling of the grinding media. Cole Parmer Cat. No. EW-04172-02  
Milling jar sleeve: Milling jar sleeve, Cole Parmer Cat. No. EW-04172-12  
Grinding media: Zirconia grinding media, 3/8" x 3/8. Cole Parmer Cat. No. EW-04158-10. About 2.37kg (750 pieces) of the grinding media were used per milling jar.  
Sieve: USA standard test sieve, No 10. (2mm). Stainless steel frame and wire, 8" diameter. Cole Parmer Cat. No. EW-59984-01.

### **Approach**

The chemical precursors were first evaluated to determine the molar amount of metal per unit weight of precursor. The established molar quantities were then used to determine the precursor quantities yielding the desired metal ratio. The respective precursors were weighed and mixed, calcined, and finally milled following the methods prescribed in the Kamauchi patent. The synthesized materials were analyzed for phase content by X-ray diffraction and particle size by several methods.

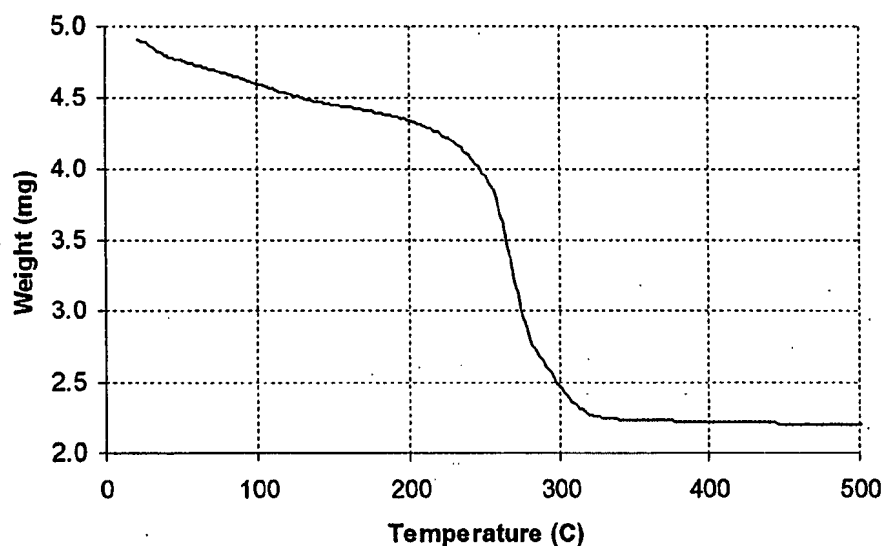
## **RESULTS AND DISCUSSION**

### **Precursor Analysis**

The cobalt (II) carbonate hydrated as purchased contains unknown amount of hydrated water. It is necessary to determine the water content in order to achieve an accurate stoichiometry.

Before the analysis, it is necessary to allow the cobalt (II) carbonate sample to reach equilibrium with normal lab atmosphere so that no water will be gained or lost during sample handling. To achieve this, about 20 g of cobalt (II) carbonate was placed on a dish and exposed to normal lab atmosphere for 14 hours. Then the exposed cobalt (II) carbonate was analyzed with TGA (thermogravimetric analyzer) to determine the water content from the weight loss. The TGA ramp rate was 10C/min. The atmosphere was 4% H<sub>2</sub> in N<sub>2</sub>. The result is shown in Figure 1.

Figure 1. TGA Curve of Cobalt (II) Carbonate Hydrated



The total wt loss from room temp to 500C was about 54.8%, corresponding to CoCO<sub>3</sub> 8.0 H<sub>2</sub>O (MW= 262.9). The amount of water in excess of the amount corresponding to the known hexa-hydrated form (see, for example "Merck Index") is probably due to absorbed water. Since water of hydration does not form with Li<sub>2</sub>CO<sub>3</sub> or FeO, and the P precursor was in liquid form, this analysis was not required to generate the necessary molar quantities of lithium, iron, or phosphorous per gram of their respective precursors.

### Synthesis of materials

The respective precursor chemicals were used for the synthesis of Li-Co-PO<sub>4</sub> and LiFePO<sub>4</sub> according to the teachings of the Kamauchi patent. Note that the precursor mixing method used in this experiment, grinding in a mortar and pestle, is more detailed and thorough than that described in the Kamauchi patent (see Appendix A). The mortar and pestle mixing employed in this experiment tends to reduce precursor particle size. Therefore, this approach will help minimize product particle size thus making the experiment more favorable towards achieving the results asserted in the Kamauchi patent.

### Synthesis of Li-Co-PO<sub>4</sub> mixed-phase material

According to the Kamauchi patent, it is understood that the product, hereafter referred to as Li-Co-PO<sub>4</sub> positive electrode material mix, is not a pure phase, but is a mixture of lithium phosphate, lithium cobalt phosphate, and lithium cobalt oxide. The amounts of

starting materials actually used in this experiment are shown in Table 1 and yielded a Li:Co:P atomic (mole) ratio of 2:1:1. The atomic ratio used matches that used in Example 1 of the Kamauchi patent (Appendix A).

Table 1. Amounts of Starting Materials for the Synthesis of Li-Co-PO<sub>4</sub> Material Mix

Materials	Molar mass	Wt (g) used	Moles	Atomic ratio
Li <sub>2</sub> CO <sub>3</sub>	73.88	4.984	0.06746	2.00
CoCO <sub>3</sub> 8.0 H <sub>2</sub> O	262.9	17.75	0.06752	1.00
H <sub>3</sub> PO <sub>4</sub> , 85% solution	98.00	7.785	0.06752	1.00

Li<sub>2</sub>CO<sub>3</sub> and CoCO<sub>3</sub> 8.0 H<sub>2</sub>O were weighed out and mixed with mortar and pestle for about 10 minutes. After grinding, the color was uniformly pink. Then phosphoric acid was added and mixing continued for another 20 minutes. Within a few minutes after adding phosphoric acid, foaming due to generation of CO<sub>2</sub> was observed. After the mixing, the power appeared dry. The color was pink.

The mix was then placed in a crucible and heated in the furnace. The temperature was ramped up at 10 C/min to 900 C, then held at 900 C for 24 hours. The weight of the reaction mix before heating was 29.535g. The weight of the product mix after heating was 17.382g. After heating, the product was in the form of a soft cake of powder. The color of the product was dark gray. The product was later ground and milled, as described below.

#### Synthesis of LiFePO<sub>4</sub> material

According to a journal article (Padhi, 1997, see Appendix B), the mole ratio of Li, Fe and P should be 1:1:1. The amounts of starting materials actually used in this experiment for the synthesis of LiFePO<sub>4</sub> are shown in Table 2.

Table 2. Amount of Starting Materials for the Synthesis of LiFePO<sub>4</sub>

Materials	Molar mass	Wt (g) used	Moles	Atomic ratio
Li <sub>2</sub> CO <sub>3</sub>	73.88	4.889	0.06617	1.00
FeO	71.85	9.511	0.13237	1.00
H <sub>3</sub> PO <sub>4</sub> , 85% solution	98	15.31	0.1328	1.00

Li<sub>2</sub>CO<sub>3</sub> and FeO were first weighed out and ground together with mortar and pestle for 20 minutes. After grinding, the color was uniformly gray. Then H<sub>3</sub>PO<sub>4</sub> was added. Gas (presumably CO<sub>2</sub>) was generated. After mixing of the above material, the material was dark gray and mud-like. The material was heated under nitrogen at 300°C for one hour. After heating, the material forms brittle lumps. The color was not uniform, from light gray to dark gray. The material was then ground with a mortar and pestle. Then the material was further heated under nitrogen at 800°C for 24 hours. After heating, the product was in the form of a sintered hard cake. The product color was not uniform,

from gray to beige. Some of the material adhered to the crucible tightly and could not be collected. The product was also later ground and milled, as described below.

### **Grinding of materials**

The Li-Co-PO<sub>4</sub> positive electrode material mix and the LiFePO<sub>4</sub> were ground using the same method but in two separated jars. The method used followed the teachings of Examples 10, 11, and 12 from the Kamauchi patent. The grinding jar was charged with 2.37kg (750 pieces) of grinding media. The material to be ground was added to the jar. In the case of LiCoPO<sub>4</sub>, the soft cake of material from the heating was crushed by hand and added to the milling jar. In the case of LiFePO<sub>4</sub>, the hard cake of material from the heating was crushed with mortar and pestle until the particle size was less than about 1mm, then added to the milling jar. The jar mill was turned on and adjusted to 150+/-7 rpm. After 24 hours of grinding, the powder was separated from the grinding media with a coarse (2mm) sieve. After grinding, the color of the Li-Co-PO<sub>4</sub> positive electrode material mix powder was dark gray. The color of the LiFePO<sub>4</sub> powder was grayish beige.

### **Phase Analysis via X-ray diffraction**

X-ray diffraction measurements were performed on the synthesized and ground materials. The X-ray diffraction patterns are shown in Figures 2 and 3. The pattern of the Li-Co-PO<sub>4</sub> material mix did not match that of LiCoPO<sub>4</sub> from literature. This was expected since it was a mixture. The pattern of the LiFePO<sub>4</sub> material matched XRD patterns for LiFePO<sub>4</sub> in the literature (stick pattern shown by black lines in Figure 3), but some impurity phases could be seen.

Figure 2. X-ray Diffraction Pattern of Li-Co-PO<sub>4</sub> Mixed Phase Material

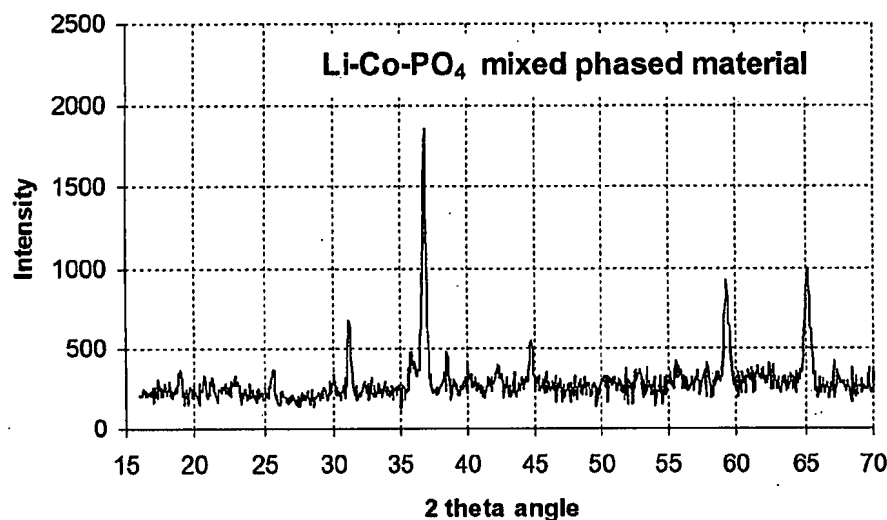
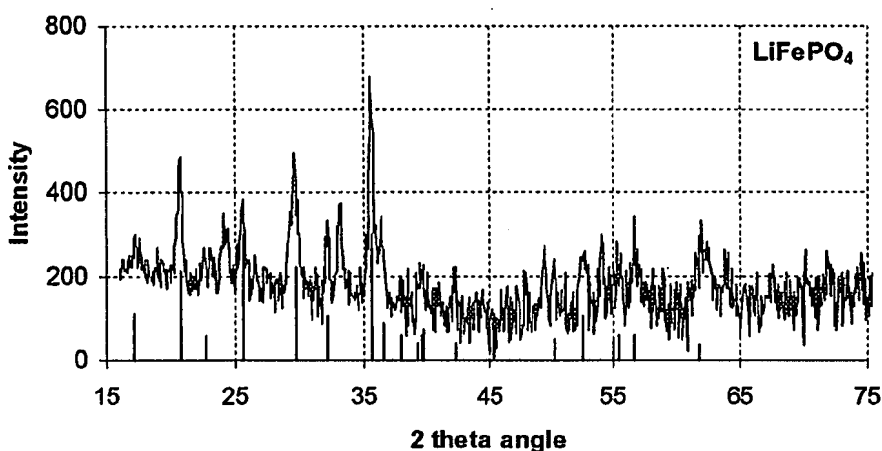


Figure 3. X-ray Diffraction Pattern of  $\text{LiFePO}_4$  Material



#### Particle size analysis

Attempts were made to measure the particle size distribution with the Malvern Zetasizer ZEN3600 particle size analyzer. Approximately 0.1 g of the Li-Co- $\text{PO}_4$  mixed phase sample after 24 hour grinding was added to 20 mL of water. The mix was shaken by hand for 1 minute and sonicated in an ultrasonic bath for 30 minutes. However, during the duration (about 2 minutes) of analysis, a significant portion of the sample precipitated. The Malvern Zetasizer ZEN3600 particle size analyzer is designed for particles small enough not to precipitate out during measurement even without stirring. The fact that Li-Co- $\text{PO}_4$  mixed phase powder precipitated indicated that the particles were too large for the instrument. Because of this difficulty, samples of both the Li-Co- $\text{PO}_4$  mixed phase powder and  $\text{LiFePO}_4$  powder were sent to Micromeritics Analytical Services<sup>1</sup> for particle size analysis by a light scattering technique performed with a Micromeritics Saturn DigiSizer 5200 Particle size analyzer (which has a larger maximum size range than the ZEN3600). General descriptions of the analysis techniques available at Micromeritics are given in Appendix C. Standard method 520-01 (non-aqueous liquid dispersion) was chosen as the method. Isopropanol was chosen as the liquid for two reasons: (1) Isopropanol wets the samples very well. (2) All components, including possible impurities, in the samples are expected to be insoluble in isopropanol.

In the preparation of the dispersion, 2.2g of the sample was added to 80 mL of isopropanol. The dispersion was sonicated using a high intensity (100 W) ultrasonic probe for one minute in order to break any agglomerates of particles. An ultrasonic probe (instead of an ultrasonic bath) was used because of its much higher intensity. The analysis was done twice for each sample. The results reported here are the average of the two analyses. The particle size distribution can be shown as a volume distribution, or as a number distribution. The difference and relationship between the two is explained in Appendix D. The NanoGram patent application describes particle size distributions with

<sup>1</sup> Micromeritics Analytical Services, [www.particletesting.com](http://www.particletesting.com), One Micromeritics Drive, Norcross, Georgia 30093-1877. (770)772-3630



respect to a number distribution. However, it is also common to describe a particle size distribution with respect to volume distribution. Therefore, the data in this experiment is provided both ways. For the two samples, the particle size volume distributions are shown graphically in Figures 4 and 5. The particle size number distributions are shown graphically in Figures 6 and 7. The numerical values of cumulative volume fraction are shown in Tables 3 and 4.

Figure 4. Particle Size Volume Distribution of Li-Co-PO<sub>4</sub> Mixed-Phase Material

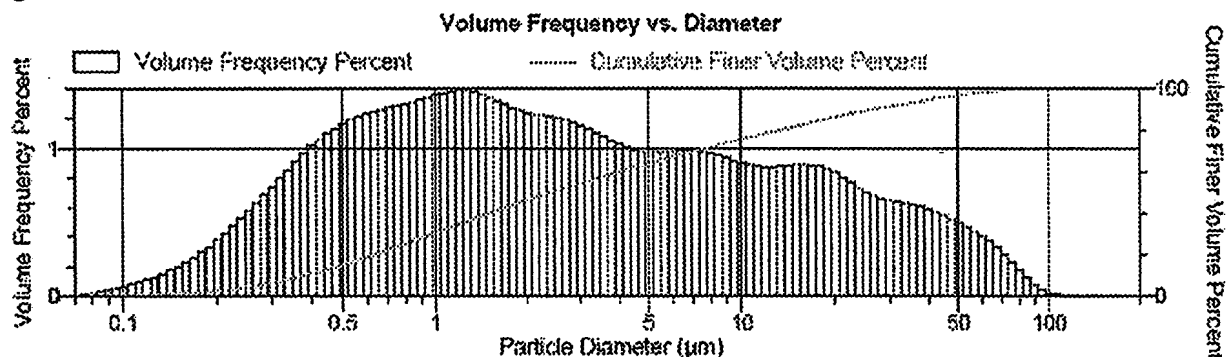


Figure 5. Particle Size Volume Distribution of LiFePO<sub>4</sub> Material

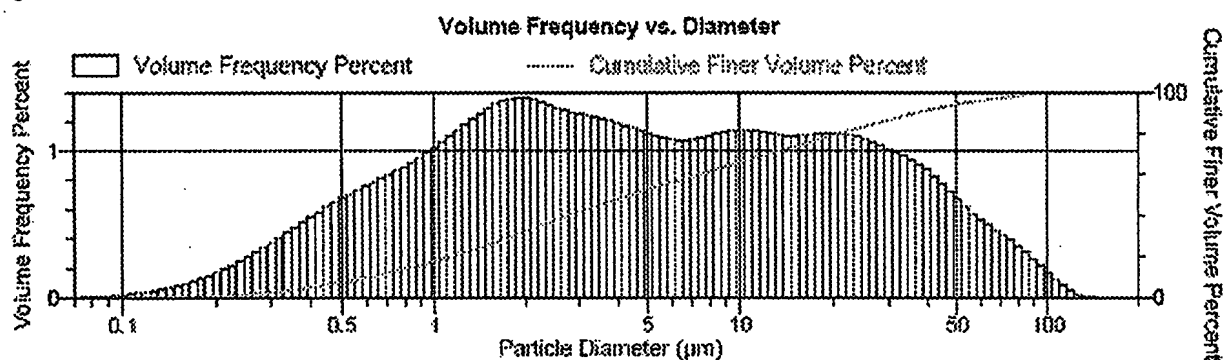


Figure 6. Particle Size Number Distribution of Li-Co-PO<sub>4</sub> Mixed-Phase Material

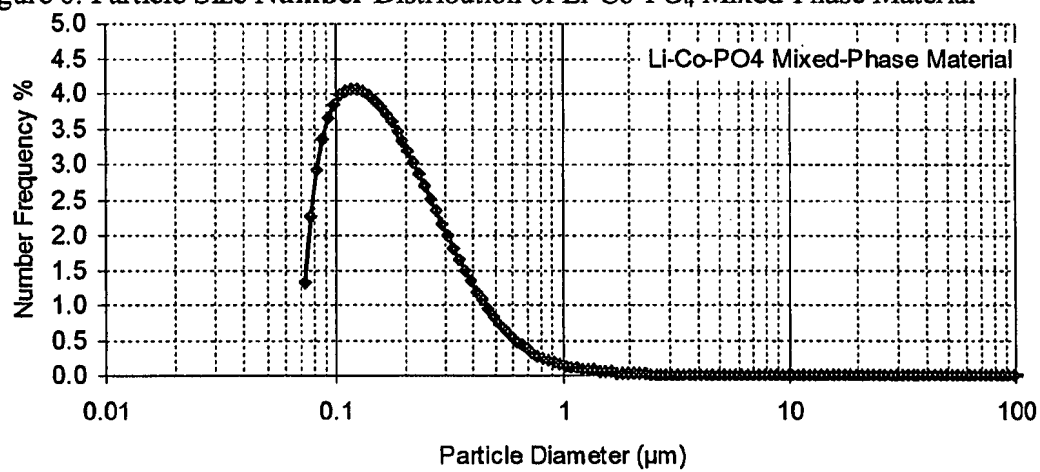


Figure 7. Particle Size Number Distribution of LiFePO<sub>4</sub> Material

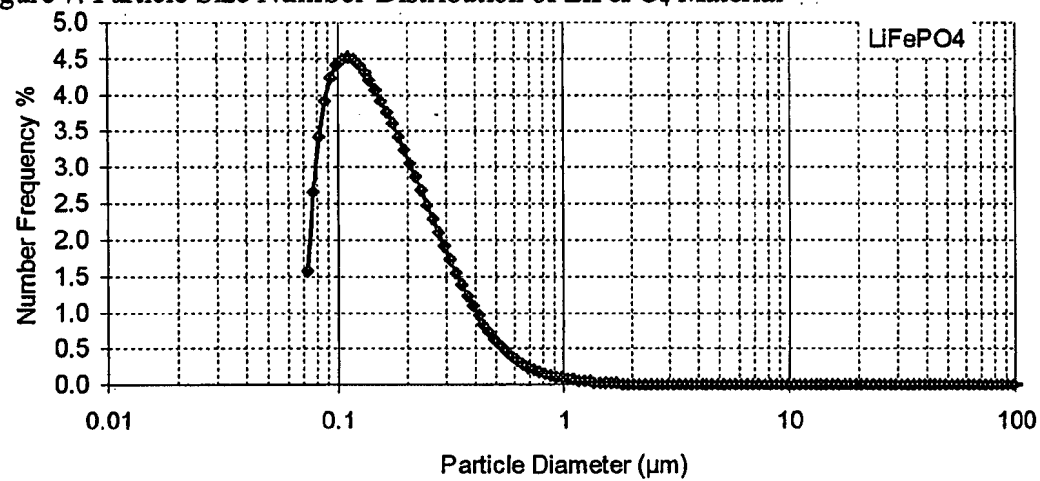


Table 3. Cumulative Volume Fractions of Li-Co-PO<sub>4</sub> Mixed-Phase Material  
Smaller than a Particular Particle Size from Two Separate Measurement Runs.

Particle size (diameter in $\mu\text{m}$ )	% volume smaller than particle size			
	Test 1	Test 2	Average	Standard Deviation
0.073	0.00%	0.00%	0.00%	0.00%
0.082	0.01%	0.01%	0.01%	0.00%
0.092	0.02%	0.04%	0.03%	0.01%
0.103	0.05%	0.08%	0.07%	0.02%
0.116	0.10%	0.15%	0.12%	0.04%
0.130	0.17%	0.25%	0.21%	0.05%
0.146	0.28%	0.38%	0.33%	0.07%
0.164	0.43%	0.56%	0.50%	0.09%
0.184	0.65%	0.80%	0.73%	0.11%
0.206	0.95%	1.12%	1.04%	0.12%
0.231	1.35%	1.54%	1.44%	0.13%
0.260	1.86%	2.06%	1.96%	0.14%
0.291	2.51%	2.70%	2.61%	0.14%
0.327	3.30%	3.48%	3.39%	0.13%
0.367	4.23%	4.40%	4.32%	0.12%
0.412	5.31%	5.46%	5.38%	0.11%
0.462	6.52%	6.65%	6.59%	0.10%
0.518	7.85%	7.98%	7.91%	0.09%
0.581	9.28%	9.41%	9.35%	0.09%
0.652	10.81%	10.95%	10.88%	0.10%
0.732	12.43%	12.60%	12.52%	0.12%
0.821	14.16%	14.35%	14.26%	0.13%
0.921	16.01%	16.22%	16.12%	0.15%
1.034	18.01%	18.23%	18.12%	0.15%
1.160	20.17%	20.38%	20.27%	0.15%
1.302	22.48%	22.70%	22.59%	0.15%
1.460	24.95%	25.18%	25.06%	0.17%
1.639	27.53%	27.80%	27.66%	0.19%
1.839	30.19%	30.51%	30.35%	0.22%
2.063	32.89%	33.25%	33.07%	0.25%
2.315	35.59%	35.95%	35.77%	0.25%
2.597	38.26%	38.57%	38.41%	0.22%
2.914	40.88%	41.12%	41.00%	0.17%
3.269	43.45%	43.62%	43.53%	0.12%

Particle size (diameter in $\mu\text{m}$ )	% volume smaller than particle size			
	Test 1	Test 2	Average	Standard Deviation
3.668	45.95%	46.08%	46.02%	0.09%
4.116	48.38%	48.48%	48.43%	0.07%
4.618	50.72%	50.82%	50.77%	0.07%
5.182	52.98%	53.08%	53.03%	0.07%
5.814	55.17%	55.27%	55.22%	0.07%
6.523	57.32%	57.42%	57.37%	0.07%
7.319	59.49%	59.58%	59.53%	0.06%
8.213	61.72%	61.77%	61.75%	0.04%
9.215	64.01%	64.02%	64.02%	0.01%
10.339	66.31%	66.31%	66.31%	0.00%
11.600	68.59%	68.59%	68.59%	0.00%
13.016	70.82%	70.84%	70.83%	0.02%
14.604	73.03%	73.06%	73.04%	0.02%
16.386	75.25%	75.27%	75.26%	0.01%
18.386	77.50%	77.50%	77.50%	0.00%
20.629	79.76%	79.74%	79.75%	0.01%
23.146	82.00%	81.98%	81.99%	0.02%
25.970	84.18%	84.16%	84.17%	0.01%
29.139	86.27%	86.26%	86.27%	0.01%
32.695	88.27%	88.26%	88.27%	0.01%
36.684	90.19%	90.17%	90.18%	0.01%
41.160	91.98%	91.95%	91.96%	0.02%
46.182	93.58%	93.55%	93.56%	0.03%
51.817	94.96%	94.94%	94.95%	0.02%
58.140	96.12%	96.13%	96.12%	0.01%
65.234	97.08%	97.15%	97.11%	0.05%
73.194	97.89%	98.03%	97.96%	0.10%
82.125	98.57%	98.76%	98.67%	0.13%
92.146	99.13%	99.33%	99.23%	0.14%
103.389	99.54%	99.71%	99.63%	0.12%
116.005	99.82%	99.92%	99.87%	0.07%
130.159	99.95%	99.99%	99.97%	0.03%
146.041	100.00%	100.00%	100.00%	0.00%

From the table, for example, only 0.07% of the volume of the powder is in particles smaller than 0.103 $\mu\text{m}$ , 1.04% smaller than 0.206 $\mu\text{m}$ , 7.91% smaller than 0.518 $\mu\text{m}$ , 18.12% smaller than 1.034 $\mu\text{m}$ , and 33.07% smaller than 2.063 $\mu\text{m}$ . The reproducibility of the two tests were excellent, as indicated by the small standard deviation.

Table 4. Cumulative Volume Fractions of LiFePO<sub>4</sub> Material Smaller than a Particular Particle Size from Two Separate Measurement Runs.

Particle size (diameter in $\mu\text{m}$ )	% volume smaller than particle size				Particle size (diameter in $\mu\text{m}$ )	% volume smaller than particle size			
	Test 1	Test 2	Average	Standard deviation		Test 1	Test 2	Average	Standard deviation
0.073	0.00%	0.00%	0.00%	0.00%	2.914	54.18%	54.23%	54.21%	0.04%
0.082	0.03%	0.03%	0.03%	0.00%	3.269	56.48%	56.51%	56.50%	0.02%
0.092	0.09%	0.10%	0.09%	0.01%	3.668	58.67%	58.69%	58.68%	0.02%
0.103	0.19%	0.22%	0.20%	0.02%	4.116	60.74%	60.77%	60.76%	0.02%
0.116	0.35%	0.39%	0.37%	0.03%	4.618	62.74%	62.77%	62.75%	0.02%
0.130	0.57%	0.62%	0.60%	0.04%	5.182	64.69%	64.72%	64.71%	0.02%
0.146	0.88%	0.95%	0.91%	0.05%	5.814	66.64%	66.67%	66.66%	0.03%
0.164	1.29%	1.37%	1.33%	0.06%	6.523	68.59%	68.64%	68.62%	0.04%
0.184	1.83%	1.93%	1.88%	0.07%	7.319	70.54%	70.62%	70.58%	0.06%
0.206	2.52%	2.64%	2.58%	0.08%	8.213	72.47%	72.57%	72.52%	0.07%
0.231	3.40%	3.53%	3.47%	0.09%	9.215	74.36%	74.46%	74.41%	0.07%
0.260	4.49%	4.62%	4.56%	0.09%	10.339	76.21%	76.28%	76.24%	0.05%
0.291	5.80%	5.94%	5.87%	0.09%	11.600	78.02%	78.05%	78.04%	0.02%
0.327	7.35%	7.48%	7.42%	0.09%	13.016	79.81%	79.81%	79.81%	0.00%
0.367	9.14%	9.25%	9.19%	0.08%	14.604	81.60%	81.58%	81.59%	0.01%
0.412	11.13%	11.23%	11.18%	0.07%	16.386	83.38%	83.37%	83.37%	0.01%
0.462	13.30%	13.39%	13.34%	0.06%	18.386	85.12%	85.14%	85.13%	0.01%
0.518	15.61%	15.69%	15.65%	0.06%	20.629	86.80%	86.84%	86.82%	0.03%
0.581	18.02%	18.10%	18.06%	0.05%	23.146	88.37%	88.42%	88.40%	0.03%
0.652	20.50%	20.58%	20.54%	0.06%	25.970	89.83%	89.85%	89.84%	0.02%
0.732	23.02%	23.11%	23.07%	0.06%	29.139	91.19%	91.19%	91.19%	0.00%
0.821	25.59%	25.69%	25.64%	0.07%	32.695	92.50%	92.48%	92.49%	0.02%
0.921	28.22%	28.33%	28.28%	0.08%	36.684	93.77%	93.73%	93.75%	0.03%
1.034	30.92%	31.03%	30.97%	0.08%	41.160	94.95%	94.93%	94.94%	0.02%
1.160	33.67%	33.78%	33.72%	0.08%	46.182	96.04%	96.04%	96.04%	0.00%
1.302	36.45%	36.55%	36.50%	0.07%	51.817	97.01%	97.05%	97.03%	0.03%
1.460	39.20%	39.29%	39.24%	0.06%	58.140	97.87%	97.95%	97.91%	0.05%
1.639	41.87%	41.95%	41.91%	0.06%	65.234	98.64%	98.73%	98.68%	0.06%
1.839	44.43%	44.51%	44.47%	0.06%	73.194	99.26%	99.34%	99.30%	0.06%
2.063	46.91%	47.00%	46.95%	0.06%	82.125	99.70%	99.75%	99.72%	0.04%
2.315	49.36%	49.44%	49.40%	0.06%	92.146	99.93%	99.94%	99.93%	0.01%
2.597	51.80%	51.87%	51.83%	0.05%	103.389	100.00%	100.00%	100.00%	0.00%
					109.515	100.00%	100.00%	100.00%	0.00%

From the table, for example, only 0.20% of the volume of the powder is in particles smaller than 0.103 $\mu\text{m}$ , 2.58% smaller than 0.206 $\mu\text{m}$ , 15.65% smaller than 0.518 $\mu\text{m}$ , 30.97% smaller than 1.034 $\mu\text{m}$ , and 46.95% smaller than 2.063 $\mu\text{m}$ . The reproducibility of the two tests were excellent, as indicated by the small standard deviation.

Table 5. Cumulative **Number** Fractions of Li-Co-PO<sub>4</sub> Mixed-Phase Material  
Smaller than a Particular Particle Size from Two Separate Measurement Runs.

Particle size (diameter in $\mu\text{m}$ )	% number smaller than particle size	Particle size (diameter in $\mu\text{m}$ )	% number smaller than particle size
0.075	1.33%	0.671	97.27%
0.080	3.60%	0.711	97.63%
0.085	6.52%	0.753	97.95%
0.090	9.88%	0.798	98.22%
0.095	13.54%	0.845	98.46%
0.100	17.39%	0.895	98.67%
0.106	21.36%	0.948	98.85%
0.113	25.39%	1.005	99.01%
0.119	29.44%	1.064	99.15%
0.126	33.49%	1.127	99.27%
0.134	37.51%	1.194	99.38%
0.142	41.48%	1.265	99.47%
0.150	45.37%	1.340	99.55%
0.159	49.18%	1.419	99.62%
0.169	52.89%	1.503	99.68%
0.179	56.49%	1.592	99.73%
0.189	59.96%	1.686	99.77%
0.200	63.29%	1.786	99.81%
0.212	66.47%	1.892	99.84%
0.225	69.50%	2.004	99.87%
0.238	72.36%	2.123	99.89%
0.252	75.05%	2.249	99.91%
0.267	77.57%	2.382	99.92%
0.283	79.91%	2.523	99.94%
0.300	82.08%	2.673	99.95%
0.318	84.07%	2.831	99.96%
0.336	85.89%	2.999	99.96%
0.356	87.55%	3.177	99.97%
0.378	89.05%	3.365	99.97%
0.400	90.39%	3.564	99.98%
0.424	91.59%	3.776	99.98%
0.449	92.66%	3.999	99.99%
0.475	93.61%	4.236	99.99%
0.503	94.44%	4.487	99.99%
0.533	95.17%	4.753	99.99%
0.565	95.81%	5.035	99.99%
0.598	96.36%	5.333	99.99%
0.634	96.85%	5.649	99.99%
		5.984	100.00%

From the table, for example, only 17.39% of the number of particles are smaller than 0.100 $\mu\text{m}$ , and 63.29% smaller than 0.200 $\mu\text{m}$ .

Table 6. Cumulative Number Fractions of LiFePO<sub>4</sub> Material Smaller than a Particular Particle Size from Two Separate Measurement Runs.

Particle size (diameter in $\mu\text{m}$ )	% number smaller than particle size	Particle size (diameter in $\mu\text{m}$ )	% number smaller than particle size
0.075	1.57%	0.598	97.77%
0.080	4.24%	0.634	98.11%
0.085	7.65%	0.671	98.40%
0.090	11.57%	0.711	98.65%
0.095	15.79%	0.753	98.86%
0.100	20.20%	0.798	99.03%
0.106	24.70%	0.845	99.18%
0.113	29.22%	0.895	99.31%
0.119	33.70%	0.948	99.42%
0.126	38.12%	1.005	99.52%
0.134	42.45%	1.064	99.59%
0.142	46.66%	1.127	99.66%
0.150	50.74%	1.194	99.72%
0.159	54.67%	1.265	99.77%
0.169	58.44%	1.340	99.81%
0.179	62.05%	1.419	99.84%
0.189	65.47%	1.503	99.87%
0.200	68.72%	1.592	99.89%
0.212	71.78%	1.686	99.91%
0.225	74.65%	1.786	99.92%
0.238	77.32%	1.892	99.94%
0.252	79.80%	2.004	99.95%
0.267	82.10%	2.123	99.96%
0.283	84.20%	2.249	99.96%
0.300	86.11%	2.382	99.97%
0.318	87.85%	2.523	99.97%
0.336	89.42%	2.673	99.98%
0.356	90.82%	2.831	99.98%
0.378	92.06%	2.999	99.99%
0.400	93.17%	3.177	99.99%
0.424	94.14%	3.365	99.99%
0.449	94.98%	3.564	99.99%
0.475	95.72%	3.776	99.99%
0.503	96.36%	3.999	99.99%
0.533	96.90%	4.236	100.00%
0.565	97.37%		

From the table, for example, only 20.20% of the number of particles are smaller than 0.100 $\mu\text{m}$ , and 68.72% smaller than 0.200 $\mu\text{m}$ .

## CONCLUSIONS

In this experiment, Li-Co-PO<sub>4</sub> mixed-phase material were synthesized using methods taught in United States Patent #5,538,714 (the "Kamauchi Patent"), and LiFePO<sub>4</sub> material was synthesized using the approaches of the Goodenough research group. Both materials were ground using the method in the Kamauchi Patent. After grinding, both powders were analyzed for particle size distribution. The results clearly indicated that the particles have a broad particle size distribution.

## APPENDIX

### A: US patent 5,538,814 - Lithium Secondary Batteries, Kamauchi et al.

For reference, the relevant parts of US Patent # 5,538,814 (the Kamauchi patent) are highlighted below

#### Example 1

Predetermined amounts of lithium carbonate, basic cobalt carbonate, and 85% phosphoric acid aqueous solution were weighed to fulfill an atomic ratio of Li:Co:P=2:1:1, sufficiently mixed in an alumina crucible, and heated at 900° C in an electric oven for twenty-four hours.

The heated product was identified by X-ray powder diffraction analysis with the use of JCPDS cards. The results of the X-ray analysis showed that the product contained lithium phosphate, lithium-cobalt phosphate, and cobalt oxide at a molar ratio of Li:Co:P=1:0.5:0.5

#### Example 10

The positive electrode active material obtained in Example 1 was further pulverized in a ball mill for 24 hours to adjust the average particle size thereof to about 0.5  $\mu\text{m}$ , and the BET specific surface area to 5  $\text{m}^2/\text{g}$ .

Twenty lithium batteries were fabricated in the same manner as in Example 1 by using this positive electrode.

#### Examples 11, 12

In the same manner as in Example 10 except that the average particle size, and the BET specific surface area of the positive electrode active material were changed as shown in Table 3 by varying the pulverizing time in a ball mill, 20 lithium batteries were fabricated in each Example.

The lithium batteries of Example 10-12 were charged in the same manner as above, and discharge capacity was determined, the results of which are shown in Table 7 wherein the figures are average values.

Partial Table 7

	Active material average particle size ( $\mu\text{m}$ )	BET specific surface area ( $\text{m}^2/\text{g}$ )
Example 10	0.5	5
Example 11	5	1
Example 12	0.01	800

#### **B. Padhi (1997) article on Phospho-olivines**

The original publication on the use of  $\text{LiFePO}_4$  for lithium secondary batteries is "Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries", by A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, Journal of The Electrochemical Society, Vol. 144, issue 4, page 1188-1193 (1997). A copy of this article is attached. For completeness, the most relevant parts of the article are highlighted below.

#### Experimental

$\text{LiMPO}_4$  ( $\text{M} = \text{Mn, Fe, Co, or Ni}$ ) compounds were prepared by direct solid-state reaction of stoichiometric amounts of  $\text{M(II)-acetates}$ , ammonium phosphate, and lithium carbonate.  $\text{LiFePO}_4$  and  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$  ( $x = 0.25, 0.50, \text{ and } 0.75$ ) were synthesized in inert atmosphere to prevent the formation of  $\text{Fe}^{3+}$  compounds as impurities. The intimately ground stoichiometric mixture of the starting materials was first decomposed at 300 to 350°C to drive away the gases. The mixture was then reground and returned to the furnace at 800°C for 24 h before being cooled slowly to room temperature.

#### **C. Particle Size Analysis by Laser Light Scattering conducted a Micromeritics**

Laser light scattering technique utilizes Mie and Fraunhofer Theories to determine particle size distribution from a light scattering pattern. Micromeritics has both the Saturn Digisizer 5200 and the Mastersizer 2000 available for this technique. The Mastersizer 2000 is capable of performing particle size distribution using either the dry dispersion module or wet dispersion module. The Saturn Digisizer 5200 is the highest resolution instrument available, capable of distinguishing small differences in samples. The particle size range is 0.02  $\mu\text{m}$  to 2000  $\mu\text{m}$ .

Available standard tests:

520 - 00

Particle size analysis using an aqueous dispersion. A distribution of particle size diameter is reported between 0.1 to 1000 micrometers. The technique requires at least 2 grams of dry sample material.

520 - 01

Particle size analysis using a non-aqueous dispersion. A distribution of particle size diameter is reported between 0.1 to 1000 micrometers. The technique requires at least 2 grams of dry sample material.

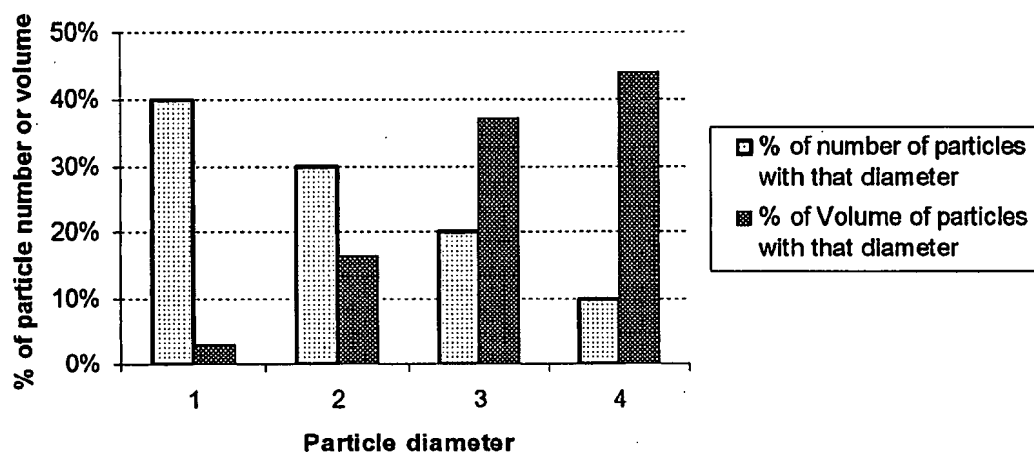


#### D. Relationship between volume distribution and number distribution

The result of particle size analysis is expressed as a distribution, which states what percentage of the powder sample is in each size range. If the percentage is based on volume of particles, the distribution is a volume distribution. Alternatively, if the percentage is based on number of particles, the distribution is a number distribution. The relationship between the two distributions is illustrated a very simple example.

Assuming there are 4 particles with diameter 1 $\mu$ m, 3 particles with diameter 2 $\mu$ m, 2 particles with diameter 3 $\mu$ m, and 1 particle with diameter 4 $\mu$ m. The volume distribution and the number distribution are calculated in the table below, and shown in the figure below.

Particle Diameter	Number of particles	% of number of particles with that diameter	Vol of each particle	Sum of Vol of particles with that diameter	% of Vol of particles with that diameter
1	4	40%	0.524	2.09	3%
2	3	30%	4.189	12.57	16%
3	2	20%	14.137	28.27	37%
4	1	10%	33.510	33.51	44%
Sum of all particles	10			76.45	



From the example above, it can be understood that number distribution tends to show higher % for smaller particles, and volume distribution tends to show higher % for larger particles. Based on an assumption of uniform particle shape, each distribution can be converted from one representation to the other. As presented above, the particles were assumed to be spherical.

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### Work Experience:

**November 2005 to Present.** NanoGram Corporation, San Jose, CA. Director, Electrochemical Applications

- Identify new opportunities for applying NanoGram's NanoParticle Manufacturing (NPM™) and Laser Reactive Deposition (LRD™) technology in advanced applications based on electrochemical technology. Areas include batteries, fuel cells, sensors, ultracapacitors, drug delivery, and windows.
- Provide technical strategy and value proposition for Corporate Strategy Team's Opportunity Analysis.
- Technical point-of-contact for US, European, and Japanese customers.
- Manage application developments by leading process development efforts, defining process equipment requirements, and identifying areas for patent coverage. Compose and manage department budget.

**August 2003 to November 2005.** Kainos Energy Corporation, San Jose, CA. Founder and Sr. Vice President, Engineering

- Overall accountability for operations, technical assessment, strategic planning, and fund raising to commercialize fuel cell components and stacks based on novel, LRD™-based approach to fuel cell manufacturing. Lead inventor on LRD™ route to fuel cell manufacturing and enabled novel designs.
- Lead design of equipment and facilities to perform proof of concept for LRD™-process based Solid Oxide Fuel Cell (SOFC) fabrication.
- Wrote successful funding proposal to National Science Foundation for development of SOFC fabrication
- Established connections with several companies (public and private), national labs, and materials characterization labs to support SOFC development.

**February 2003 to August 2003.** Consultant to NanoGram Corporation, San Jose, CA.

- Explored new applications of NanoGram's LRD™ and NPM™ technology. Created value proposition for fuel cell and derivative applications. Efforts led to formation of NanoGram subsidiary, Kainos Energy Corporation, in Aug. 2003.

**August 1998 to February 2003.** NeoPhotonics Corporation and NanoGram Corporation, San Jose, CA.

- Participated in efforts to secure more than \$60 M in venture capital funding comprising lab tours, technology due diligence, and technical presentations to private and corporate investors.
- Director, Materials & Process Engineering (Aug 2002 – Feb 2003). Managed 19 person organization developing novel processes for advanced planar lightwave circuits. Composed operating budget and CapEx plans.
- Manager, Advanced Materials & Methods Group (Dec 2001 – Aug 2002). Built new department to develop novel processes for optical component manufacturing. Designed and budgeted \$0.5M Advanced Materials Development Laboratory. Continued as technical lead for planar amplifier development.
- Senior Scientist, Optical Components (July 2000 – Dec 2001). Lead inventor for NanoGram/NeoPhotonics' planar amplifier technology. Provided technical input and assisted in defining NanoGram/NeoPhotonics value proposition and business strategy for active optical components.
- Senior Scientist, Nanoscale Energy Storage & Conversion Components (Aug 1998 – June 2000). Defined technical value proposition for use of nanoscale active materials in lithium ion batteries. Developed company-wide capabilities for nanoscale material processing and analysis. Led several projects' developing nanoscale active materials for lithium ion battery applications. Interfaced with US, European, and Japanese customers. Authored several development proposals.
- Technical founder, NanoGram Devices Corporation (NDC). Lead inventor of process for manufacturing nanoscale active material for implantable lithium batteries that formed basis of NDC value proposition.
- Organized & coordinated NanoGram's and NeoPhotonics' summer intern programs using university connections. Program yielded four permanent hires to engineering staff.

**August 1993 to August 1998.** Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, CA. Graduate Student Research Assistant, Environmental Energy Technologies Division.

- First to correlate degree of covalency with Mn substitution in lithium manganese spinels to explain observed property and performance differences.
- Conceptualized, designed, & implemented new project on X-ray and NMR Spectroscopic analysis of lithium rechargeable battery materials in collaboration with two other academic groups.
- Project included synthesis & characterization of metal-substituted lithium manganese oxides, electrode design, battery cell fabrication & testing.
- Authored over 10 successful proposals for experimental time at US Department of Energy synchrotrons.

- Coordinated & performed X-ray experimentation at synchrotron facilities housed at three DOE National Laboratories: Stanford Synchrotron Radiation Laboratory (Stanford Linear Accelerator Center, Palo Alto, CA), National Synchrotron Light Source (Brookhaven National Lab, Upton, NY), & Advanced Light Source (Lawrence Berkeley National Laboratory, Berkeley, CA).

May 1988 to July 1993. AlliedSignal Aerospace Systems & Equipment (now GE Power Systems), Torrance, CA. Engineer. Fuel Cell Engineering Group.

- Primary assignment as member of Solid Oxide Fuel Cell development team. Additional assignments included high-T<sub>c</sub> superconductor & whisker-reinforced ceramic composites product development team.
- Co-inventor with N.Q. Minh of thin-film tape calendaring process and stack construction method currently used in GE's SOFC program.
- Responsible for powder preparation, batching, fabrication operations, & single-cell testing for customer-supported Solid Oxide Fuel Cell (SOFC) programs.
- Designed & implemented first process database and quality-control systems for tape-calendar based SOFC component fabrication. Participated in Total Quality Management teams that lowered SOFC component development cycle time by 33%.
- Participated in customer & technical presentations as well as proposal & report writing teams.
- Obtained M.S. at UCLA part-time while working full-time.

### Education:

Ph.D. in Materials Science & Mineral Engineering; University of California, Berkeley. December 2000.

Thesis Advisor: Elton Cairns; Professor, Department of Chemical Engineering

Dissertation Title: Processing – Structure – Property – Performance Investigations of Lithium Manganese-Based Oxides for Li Rechargeable Batteries.

Minors: Chemical Engineering, Energy and Resources (ERG)

M.S. in Materials Science & Engineering; University of California, Los Angeles. December 1993.

B.S. (with High Honors) in Materials Science & Engineering; University of Florida, Gainesville. May 1988.

### Honors and Awards:

Summer 1997 Department of Energy/Electrochemical Society Summer Fellow

Fall 1997 U.C. Berkeley University Fellow

Co-winner, Graduate Student Poster Contest, 24<sup>th</sup> Annual Stanford Synchrotron Radiation Laboratory Users Meeting

1998 Daniel Cubicciotti Student Award from The San Francisco Section of The Electrochemical Society  
Salutatorian, Department of Materials Science & Engineering, University of Florida, Class of Spring 1988

Honor Societies: Alpha Sigma Mu - President, 1987 to 1988; Tau Beta Pi; Keramos; Florida Blue Key

Deans Lists: College of Liberal Arts & Sciences, U. Florida College of Engineering (4 times); National Deans List

### Professional and Other Activities:

Electrochemical Society, San Francisco Section – Chair 2005 to 2006, 2000 to 2001, Vice Chair 2004 to 2005, 1999 to 2000, Recording Secretary 1998 to 1999

Electrochemical Society – Individual Membership Committee 2005 to 2007

California Hydrogen Highway – Rollout Strategy Topic Team, Production and Delivery Subgroup

Silicon Valley Energy & Transportation Interest Group

Refereed over 15 papers for *Journal of the Electrochemical Society* and *Electrochemical & Solid State Letters*

U. Florida Lacrosse Club (1984 to 1988): President & Captain 1987 to 1988, Treasurer 1986 to 1987.

U. Florida Homecoming, University Services Division: Director 1987 to 1988, Asst. Director 1986 to 1987.

### Patent List:

#### U.S. Patents Awarded

1. Patent #6,952,504 - X.X. Bi, E.A. Nevis, R.J. Mosso, M.E. Chapin, S. Chiruvolu, S.H. Khan, S. Kumar, H.A. Lopez, Huy, N.T.T., C.R. Horne, M.A. Bryan, and E.H. Euvrard, *Three Dimensional Engineering of Planar Optical Structures*.
2. Patent #6,849,334 - C.R. Horne, P.J. DeMascarel, C.C. Honeker, B. Chaloner-Gill, H.A. Lopez, X.X. Bi, R.J. Mosso, W.E. McGovern, J.T. Gardner, S. Kumar, J.A. Gilliam, V. Pham, E.H. Euvrard, S. Chiruvolu, and J. Jur, *Optical Materials and Optical Devices*.
3. Patent #6,749,648 - S. Kumar, C.R. Horne, *Lithium Metal Oxides*.
4. Patent #6,732,435 - C.R. Horne, J. Jur, R.J. Mosso, E.H. Euvrard, and X.X. Bi, *Optical Fiber Preforms*.
5. Patent #6,482,374 - S. Kumar, H.D. Reitz, C.R. Horne, J.T. Gardner, R.J. Mosso, and X.X. Bi, *Methods for Producing Lithium Metal Oxide Particles*.

6. Patent #6,225,007 - C.R. Horne, S. Kumar, J.P. Buckley, and X.X. Bi, *Metal Vanadium Oxide Particles*.
7. Patent #6,136,287 - C.R. Horne, S. Kumar, H.D. Reitz, J. T. Gardner, and X.X. Bi, *Lithium Manganese Oxides and Batteries*.
8. Patent #5,368,667 - J.V. Guiheen, C.R. Horne, and N.Q. Minh, *Preparation of Devices That Include a Thin Ceramic Layer*.
9. Patent #5,290,642 - C.R. Horne and N.Q. Minh, *Method of Fabricating a Monolithic Solid Oxide Fuel Cell*.
10. Patent #5,162,167 - C.R. Horne and N.Q. Minh, *Apparatus and Method of Fabricating a Monolithic Solid Oxide Fuel Cell*.

Twelve U.S. and numerous PCT patent applications in fuel cell fabrication and design, nanoscale materials processing, nanoscale battery materials, nanoscale battery components, photovoltaic cell fabrication, combinatorial discovery, and nanoscale optical materials & structures.

## Journal Papers, Oral Presentations, Conference Proceedings, and Poster Presentations:

### Journal Papers

1. C.R. Horne, U. Bergmann, M.M. Grush, R.C.C. Perera, D.L. Ederer, T.A. Callcott, E.J. Cairns, and S.P. Cramer, "Electronic Structure of Chemically-Prepared  $\text{Li}_x\text{Mn}_2\text{O}_4$  Determined By Mn X-ray Absorption and Emission Spectroscopies", *Journal of Physical Chemistry B*, **104**(2000)9587-9596.
2. C.R. Horne, U. Bergmann, J. Kim, K.A. Striebel, A. Manthiram, S.P. Cramer, and E.J. Cairns, "Structural Investigations of  $\text{Li}_{1.5+x}\text{Na}_{0.5}\text{MnO}_{2.85\pm 0.12}$  Electrodes by Mn X-Ray Absorption Near Edge Spectroscopy", *Journal of The Electrochemical Society*, **147**(2000)395-398.
3. M.M. Grush, C.R. Horne, R.C.C. Perera, D.L. Ederer, S.P. Cramer, E.J. Cairns, and T.A. Callcott, "Correlating Electronic Structure with Cycling Performance of Substituted  $\text{LiMn}_2\text{O}_4$  Electrode Materials: A Study Using the Techniques of Soft X-ray Absorption and Emission", *Chemistry of Materials*, **12**(2000)659-664.
4. B. Gee, C.R. Horne, E.J. Cairns, and J.A. Reimer, "Supertransferred Hyperfine Fields at  $^7\text{Li}$ : Variable Temperature  $^7\text{Li}$  NMR Studies of  $\text{LiMn}_2\text{O}_4$ -Based Spinel", *Journal of Physical Chemistry B*, **102**(1998)10142-10149.
5. U. Bergmann, C.R. Horne, T.J. Collins, J.M. Workman, and S.P. Cramer, "Chemical Dependence of Interatomic X-ray Transition Energies and Intensities - a Study of Mn  $K\beta$ " and  $K\beta_{2,5}$  Spectra", *Chemical Physics Letters*, **302**(1999)119-124.
6. K.S. Striebel, A. Rougier, C.R. Horne, R.P. Reade, and E.J. Cairns, "Electrochemical Studies of Substituted Spinel Thin Films", *Journal of The Electrochemical Society*, **146**(1999)4339-4347.
7. U. Bergmann, M.M. Grush, C.R. Horne, P. DeMarois, J.E. Penner-Hahn, C.F. Yocum, D.W. Wright, C.E. Dubé, W.H. Armstrong, G. Christou, H.J. Eppley, and S.P. Cramer, "Characterization of the Mn Oxidation States in Photosystem II by  $K\beta$  X-ray Fluorescence Spectroscopy" *Journal of Physical Chemistry B*, **102**(1998)8350-8352.
8. S.P. Cramer, H.-X. Wang, C. Bryant, M. Legros, C.R. Horne, D. Patil, C. Ralston, and X. Wang, "Soft-Xray Absorption Spectroscopy - Applications to Bioinorganic Chemistry", *ACS Series*, **692**(1998)154-178.

### Oral Presentations

1. U.C. Berkeley NanoConference, Panel on Energy & Nano. Berkeley, CA. April 15, 2006. (Invited Panelist)
2. MIT Club of Northern California's Renewable Energy and Clean Technology Program, Panel on New Business Models in Renewable Energy. Palo Alto, CA. Nov. 3, 2005. (Invited Panelist)
3. C.R. Horne, A. Jaiswal, A. Vu, J. Zhang, L. Acosta, R.B. Lynch, J.R. Mentz, W.E. McGovern, and R.J. Mosso, "A Disruptive Laser-Based Process for Low Cost SOFC Manufacturing" at the 2005 Fuel Cell Seminar. Palm Springs, CA. Nov. 14-18, 2005.
4. C.R. Horne, "Solid Oxide Fuel Cells" at the MIT-Stanford-Berkeley Nanotechnology Forum's Alternate Energy Technologies for Tomorrow Event. Palo Alto, CA. July 12, 2005. (Invited)
5. S. Mardini\* and C.R. Horne, "Kainos Energy" at the CleanTech Venture Forum VI. San Francisco, CA. Mar. 22-23, 2005.
6. C.R. Horne, P. de Mascarel, R. Blume, J. Jur, C. Cohen-Jonathan, M. Chapin, J. Posner, W.C. Foo, C. Honeker, Q. Zhu, S. Chiruvolu, R. Mosso, and W. McGovern, "High-Rate Deposition Of Rare-Earth Doped Silicate Nanoparticles For Porous & Dense Optical Films" at the 2005 Spring Meeting of The Materials Research Society. San Francisco, CA. Mar. 28-Apr. 1, 2005.
7. C.R. Horne, "Kainos Energy" at the NanoScience Exchange's Event on Energy Technologies to Reduce Dependence on Foreign Oil. Menlo Park, CA. October 11, 2004. (Invited)
8. C.R. Horne, "Nano-Enabled Fuel Cells" at the NanoSIG Clean Energy and Nano Catalyst Conference. Menlo Park, CA. Aug. 20, 2004.
9. C. R. Horne, "Overview of Lithium Rechargeable Battery Technology & Nanomaterial Applications" at Semi-Therm20. San Jose, CA. Mar. 9-11, 2004. (Invited, Luncheon Plenary)

10. C. R. Horne, P. de Mascarel, R. Blume, S. Chiruvolu, M. Chapin, J. Jur., W. McGovern, R. Mosso, "High-Rate Deposition of Compositionally Complex Nanoparticles for Porous and Dense Films: II. Capabilities" at the 55<sup>th</sup> Pacific Coast Regional & Basic Science Division Fall Meeting of the American Ceramic Society. Oakland, CA. Oct. 19-22, 2003.
11. C. R. Horne, S. Kumar, B. Chaloner-Gill, D. Ghantous, J. Gardner, R. Mosso, N. Kambe, "Processing - Structure - Property - Performance Investigations of Nanocrystalline Materials for Lithium Rechargeable Batteries" at the 55<sup>th</sup> Pacific Coast Regional & Basic Science Division Fall Meeting of the American Ceramic Society. Oakland, CA. Oct. 19-22, 2003. (Invited)
12. C.R. Horne, "Careers in Glass – Integrated Photonic Circuits" at the 2002 Glass & Optical Materials Division Meeting of the American Ceramic Society. Pittsburgh, PA. Oct. 13-16, 2002. (Invited)
13. C.R. Horne, "Nanocrystalline Lithium Transition-Metal Oxides for Lithium Rechargeable Batteries" at the 198<sup>th</sup> Meeting of The Electrochemical Society. Phoenix, AZ. Oct. 22-27, 2000.
14. C.R. Horne, U. Bergmann, M.M. Grush, J. Kim, A. Manthiram, S.P. Cramer, K.A. Striebel, and E.J. Cairns, "Structural Studies of Lithium Insertion in Lithium Manganese Oxides" at the 196<sup>th</sup> Meeting of The Electrochemical Society. Honolulu, HI. Oct. 17-22, 1999.
15. C.R. Horne, T.J. Richardson, B. Gee, M. Tucker, M.M. Grush, U. Bergmann, K.A. Striebel, S.P. Cramer, J.A. Reimer, and E.J. Cairns, "Composition-Structure-Property-Performance Relationship in Mn-substituted  $\text{LiMn}_2\text{O}_4$ " at the 196<sup>th</sup> Meeting of The Electrochemical Society. Honolulu, HI. Oct. 17-22, 1999.
16. C.R. Horne, K.A. Striebel, E.J. Cairns, M.M. Grush, U. Bergmann, and S.P. Cramer, "Atomic & Electronic Structural Consequences of Mn-Substitution in  $\text{LiMn}_{2-x}\text{Me}_x\text{O}_4$  by X-ray Absorption and FTIR Spectroscopies" at the 1997 Fall Meeting of the Materials Research Society. Boston, MA. Dec. 1-5, 1997.
17. C.R. Horne, E.J. Cairns, U. Bergmann, S.P. Cramer, M.M. Grush, and B.J.R. Weiss, "X-ray Spectroscopic Investigations of the Atomic & Electronic Structure of  $\text{Li}_x\text{Mn}_2\text{O}_4$  for Li Rechargeable Batteries" at the 1997 Fall Meeting of the Materials Research Society. Boston, MA. Dec. 1-5, 1997.
18. C.R. Horne, N.Q. Minh, A. Amiro, T.R. Armstrong, J.R. Esopa, J.V. Guilleen, and J.J. Van Ackeren, "Monolithic Solid Oxide Fuel Cell Development: Recent Technical Progress," at the 1992 Fuel Cell Seminar. Tucson, AZ. Nov. 29-Dec. 2, 1992.

#### Conference Proceedings Papers

1. C.R. Horne, E. Ooi, R.B. Lynch, J.R. Mentz, W.E. McGovern, and R.J. Mosso, "Innovative, Laser-Based Process for Development and Manufacturing of SOFCs", in Solid Oxide Fuel Cells IX, S.C. Singhal and J. Mizusaki, eds. Quebec City, Canada, Spring 2005. The Electrochemical Society. PV 2005-07. pp. 466-75.
2. C.R. Horne, P. de Mascarel, R. Blume, J. Jur, C. Cohen-Jonathan, M. Chapin, J. Posner, W.C. Foo, C. Honeker, Q. Zhu, S. Chiruvolu, R. Mosso, and W. McGovern, "High-Rate Deposition Of Rare-Earth Doped Silicate Nanoparticles For Porous & Dense Optical Films", in Rare-Earth Doping for Optoelectronic Applications, T. Gregorkiewicz, Y. Fujiwara, M. Lipson, and J.M. Zavada, eds. San Francisco, Spring 2005. Mater. Res. Soc. Symp. Proc. 866, Paper V2.7 (2005).
3. X.X. Bi, S. Kumar, C. Horne, B. Chaloner-Gill, and R. Mosso, "Synthesis of Nanoscale Optical Materials Using Nano Particle Manufacturing (NPM™) Technology", in Optoelectronics, Materials, and Devices for Communications, T.P. Lee and Q. Wang, eds, Proc. SPIE 4580, pp. 103-111 (2001).
4. C.R. Horne, "Nanocrystalline Lithium Transition-Metal Oxides for Lithium Rechargeable Batteries" in Rechargeable Lithium Batteries, K.M. Abraham, E.S. Takeuchi, and M. Doyle, eds. Phoenix, Arizona, Fall 2000. The Electrochemical Society. PV 2000-21. pp. 1-7.
5. C.R. Horne, U. Bergmann, M.M. Grush, J. Kim, A. Manthiram, S.P. Cramer, K.A. Striebel, and E.J. Cairns, "Structural Studies of Lithium Insertion in Lithium Manganese Oxides", in Intercalation Compounds for Battery Materials, G. A. Nazri, T. Ohzuku, and M. Thackeray, eds. Honolulu, Hawaii, Fall 1999. The Electrochemical Society. PV 99-24, pp. 41-47.
6. C.R. Horne, T.J. Richardson, B. Gee, M. Tucker, M.M. Grush, U. Bergmann, K.A. Striebel, S.P. Cramer, J.A. Reimer, and E.J. Cairns, "Composition-Structure-Property-Performance Relationship in Mn-substituted  $\text{LiMn}_2\text{O}_4$ ", in Intercalation Compounds for Battery Materials, G. A. Nazri, T. Ohzuku, and M. Thackeray, eds. Honolulu, Hawaii, Fall 1999. The Electrochemical Society. PV 99-24, pp. 112-120.
7. K.A. Striebel, A. Rougier, C.R. Horne, R.P. Reade and E.J. Cairns, "Characterization Of Pulsed Laser Deposited  $\text{LiMn}_{2-x}\text{Me}_x\text{O}_4$  (Me = Co, Ni) Thin Films For Rechargeable Lithium Batteries" in Lithium Batteries, S. Surampudi and R. A. Marsh, eds. Boston, MA, Fall 1998. The Electrochemical Society. PV 98-16, pp. 263-270.
8. E.J. Cairns, C.R. Horne, B.J. Weiss, M.M. Grush, and S.P. Cramer, "X-Ray Absorption Spectroscopic Investigations of  $\text{Li}_x\text{Mn}_2\text{O}_4$ ", in Proceedings of the 2nd International Symposium on New Materials for Fuel Cells and Modern Battery Systems, Montreal, Canada, July 6-10, 1997. Savadogo, O. and Roberge, P.R., eds., École Polytechnique de Montréal. 1997. pp. 336-347.
9. N.Q. Minh and C.R. Horne, "A Novel Method for Fabricating Thin-Film Ionic & Mixed Conductors" in Proceedings of the 14th RISO International Symposium on Materials Science: High Temperature

- Electrochemical Behavior of Fast Ion & Mixed Conductors, F.W. Poulsen, J.J. Bentzen, T. Jacobsen, E. Shou, and M.J.L. Ostergard, eds. 1993, p. 520.
10. N.Q.Minh, T.R. Armstrong, J.R. Esopa, J.V. Guiheen, C.R Horne, and J.J.Van Ackeren, "Tape-Calendered Monolithic & Flat Plate Solid Oxide Fuel Cells," in Proceedings of the Third International Symposium on Solid Oxide Fuel Cells, S.C. Singhal, ed., The Electrochemical Society, Pennington, NJ, 1993, p. 801.
  11. N.Q.Minh, A. Amiro, T.R. Armstrong, J.R. Esopa, J.V. Guiheen, C.R Horne, and J.J.Van Ackeren, "Monolithic Solid Oxide Fuel Cell Development: Recent Technical Progress," in 1992 Fuel Cell Seminar Proceedings, Tucson, AZ, 1992, p. 524.
  12. N.Q.Minh, T.R. Armstrong, J.R. Esopa, J.V. Guiheen, C.R Horne, F. Liu, T.L. Stillwagon, and J.J.Van Ackeren, "Fabrication Methodologies for Monolithic Solid Oxide Fuel Cells," in Proceedings of the Second International Symposium on Solid Oxide Fuel Cells, F. Gross, P. Zegers, S.C. Singhal, and O. Yamamoto, eds., Commission of the European Communities, Brussels, 1991, p. 93.
  13. N.Q.Minh, J.V. Guiheen, C.R Horne, F. Liu, D.M. Moffatt, T.L. Stillwagon, and J.J.Van Ackeren, "Monolithic Solid Oxide Fuel Cell Technological Status," in 1990 Fuel Cell Seminar Proceedings, Phoenix, AZ, 1990, p. 524.
  14. N.Q.Minh, C.R Horne, F. Liu, D.M. Moffatt, P. Staszak, T.L. Stillwagon, and J.J.Van Ackeren, "Fabrication and Characterization of Monolithic Solid Oxide Fuel Cells," in Proceedings of the 25th IECEC, Reno, NV, 1990, p. 230.
  15. N.Q.Minh, C.R Horne, F. Liu, P. Staszak, T.L. Stillwagon, and J.J.Van Ackeren, "Forming and Processing of Monolithic Solid Oxide Fuel Cells," in Proceedings of the First International Symposium on Solid Oxide Fuel Cells, S.C. Singhal, ed., The Electrochemical Society, Pennington, NJ, 1989, p. 307.

#### Poster Presentations

1. C. R. Horne, A. Jaiswal, A. Vu, J.W. Zhang, L. Acosta, R.E. Lynch, J.R. Mentz, W.E. McGovern, and R.J. Mosso, "Innovative, Laser-Based Process For Development And Manufacturing Of Solid Oxide Fuel Cells" at SOFC-IX. Quebec City, Canada. May 16-20, 2005.
2. C.R. Horne, E. Ooi, R.E. Lynch, J.R. Mentz, W.E. McGovern, and R.J. Mosso, "A Disruptive Laser-Based Process for Low Cost Development and Manufacturing of High Performance SOFCs", at 2004 Fuel Cell Seminar. San Antonio, TX. Nov. 1-5, 2004.
3. C.R. Horne, S. Kumar, B. Chaloner-Gill, D. Ghantous, Y. Fortunak, J. Gardner, S. Chiruvolu, K. Hoang, A. Pinoli, J. Xie, H. Reitz, J. Buckley, R. Mosso, X.X. Bi, and N. Kambe, "Nanocrystalline Lithium Transition-Metal Oxides for Lithium Rechargeable Batteries via NPM™ Processing" at the NanoSIG™ nanoMaterials & Manufacturing Forum™. Menlo Park, CA. Apr. 24, 2003.
4. C.R. Horne, P. de Mascarel, R. Blume, C. Cohen-Jonathan, J. Jur, W.C. Foo, C. Honeker, M. Chapin, J. Posner, S. Chiruvolu, B. McGovern, Q. Zhu,, R. Mosso, and N. Kambe, "Laser Reactive Deposition (LRD™) Processing of Active Glass Films for Planar Waveguide Amplifiers from NanoParticulate-based Coatings" at the NanoSIG™ nanoMaterials & Manufacturing Forum™. Menlo Park, CA. Apr. 24, 2003.
5. C.R. Horne, T.J. Richardson, B. Gee, M. Tucker, M.M. Grush, U. Bergmann, K.A. Striebel, E.J. Cairns, and S.P. Cramer, "Soft X-ray Spectroscopic Studies of Mn-substituted LiMn<sub>2</sub>O<sub>4</sub>", 1998 Advanced Light Source (ALS) Users Meeting. Berkeley, CA. Apr. 1998.
6. C.R. Horne, U. Bergmann, M.M. Grush, K.A. Striebel, E.J. Cairns, and S.P. Cramer, "X-ray Spectroscopic Studies of Lithium Insertion in Lithium Manganese Oxides" at the 24<sup>th</sup> Annual Stanford Synchrotron Radiation Laboratory (SSRL) Users Meeting. Oct. 1997.

## ON K. CHANG, Ph.D.

### SUMMARY OF QUALIFICATIONS

Senior Scientist with 18 years of experience in battery related development, process and product engineering. Hands on expertise in chemical, mechanical and electronic technical areas. Strong background in analytical chemistry, battery technology and application of statistical methods.

### PROFESSIONAL EXPERIENCE

*NanoGram Corp. San Jose, CA (Technology: nano-particles by laser pyrolysis)*

#### Consultant

1/2006 – present

- Conducted grinding experiments to support a patent application
- Conducted high temperature, solid-state material synthesis.
- Conducted material characterization.
- Developed software for data processing

*Greatbatch, Inc., Fremont, CA (Technology: batter, capacitor materials by laser pyrolysis, thermal reactions)*

#### Senior Scientist

1/2004 – 12/2005

- Worked on Silver Vanadium Oxide, Barium Titanium Oxide, and Tantalum powder development programs
- Led overall developments in post-process using laser-pyrolyzed nanopowders in SVO, BTO and Ta projects.
- Improved SVO reactors resulting in 10x better temperature control.
- Designed, fabricated improved tooling for SVO process resulting in better ergonomics and efficiency.
- Maintained SVO production database and developed software for data acquisition, resulting in 75% labor saving.
- Developed software for processing of SVO cell test data, resulting in 90% labor saving.
- Led development of nano-BTO thermal process (grinding, heating), acquired equipment. Fulfilled first deliverable in 3 months, below budget.
- Led development of Ta thermal process (reduction of oxide, sintering), acquired equipment. Fulfilled first deliverable in 6 months.

*Semitec Corporation, Santa Clara, CA (Technology: Dicing blades for singulation of semiconductor dies on wafer)*

#### Process Engineer

2/2002 - 1/2004

- Worked on dicing blades for semiconductor packaging.
- Designed and built low-cost machines for production (centrifuge, burnishing machine). Machines still in used.
- Maintained drawing files for most production tooling and parts. Support other engineers.
- Automated and improved process documentation by using Visual Basic for Excel.
- Resolved production problems in plating, chemical etching, electro-polishing, metrology to ensure efficiency.
- Conducted PM, repair on machine vision systems, interferometers, laser profilers and laser markers.
- Developed new product "beveled wheel", acquired grinding machines and developed process.
- Streamlined and improved process flow for new product "BGA blade". Wrote work instructions and designed travel sheets.

*PolyStor Corporation, Livermore, CA (Technology: Lithium ion batteries with lithium nickel cobalt oxide cathode)*

#### Scientist & Program Manager

4/1998 – 12/2001

- Worked on Li ion  $\text{LiNi}_x\text{Co}_y\text{O}_2$  rechargeable cells with rigid and flexible package.
- Developed electrode coating slurry formulation and process (slurry mixing, homogenizing).
- Developed electrolyte formulation (carbonate ester solvents,  $\text{SO}_2$ , other additives)
- Developed, validated material characterization methods ( $\text{CO}_3$ , OH,  $\text{NiOOH}$ , other impurities in  $\text{LiNi}_x\text{Co}_y\text{O}_2$ , solvent and additive in coating, water in every component, particle size of powders. Side specific loading of polymer on separator. Pinholes in packing foils, gas in polymer cells).
- Uncovered previously unknown processing problems (bubbles in coating slurry, poor vacuum in drying, water pick-up in storage etc.). Developed monitoring methods.
- Product failure analysis and failure mechanism elucidation (sources of impedance, imbalance).
- Statistical analysis of production & experimental data, trouble shooting. Automated product sorting method.
- Study effects of electrode additives. Elucidate mechanism of additive effects on over-charge protection.
- Managed a \$2M NIST ATP contract for 4 months, coordinated subcontractors, wrote reports to government.

- Participated in quality improvement activities, developed product specs (OCV, impedance, cycle life, fade rate) and incoming material specs (impurities etc), negotiated with vendors.

*Next Century Power, Scotts Valley CA (Technology: Nickel zinc batteries with improved electrolyte)*

**Research Scientist**

1/1995 – 4/1998

- Worked on Ni-Zn rechargeable cells.
- Characterized cell performance (cycle, gassing behavior). Quantified H<sub>2</sub> & O<sub>2</sub> generation separately.
- Dispelled misconception in related technologies (forms of borate in electrolyte)
- Developed electrode (ZnO & Ni(OH)<sub>2</sub> based) and electrolyte (KOH based) formulation.
- Developed chemical analysis methods (carbonate in ZnO).
- Developed processes (carbonate removal in anode, pasting for both electrodes, pre-formation for cathode).
- Studied anti-gassing additives (cationic surfactants).
- Elucidated cell failure mechanisms (area vs. point short due to ZnO ppt, additive deterioration etc.).
- Worked on various negative electrode grid treatment (cleaning, Pb plating).
- Worked on H<sub>2</sub> recombination in Ni-Zn cell using fuel cell electrode.
- Designed, built low-cost power suppliers, electronic loads, cyclers for cell testing.
- Supervised temporary employees on pilot-line cell builds.

*Valence Technology, San Jose, CA (Technology: Lithium batteries with electron beam polymerized solid electrolyte)*

**Scientist**

10/1990 – 1/1995

- Awarded 16 patents related to battery technology, material characterization.
- Worked on Li-V<sub>6</sub>O<sub>13</sub> polymer electrolyte rechargeable cells.
- Developed electrode formulation (types and % of carbon, active material).
- Developed material characterization method (polymer precursors in electrolyte by HPLC, IR; Lewis acid in electrolyte by a patent method, dry box atmosphere by UV, conductivity of paste etc).
- Routine and non-routine evaluation of product performance (e.g., shape change, gassing during cycling).
- Developed non-destructive method to quantify gas inside cell package, and automatic method of sorting cells.
- Worked on cathode active material (V<sub>6</sub>O<sub>13</sub>, LiV<sub>3</sub>O<sub>8</sub>) synthesis by solid state, sol-gel methods.
- Product failure analysis and failure mechanism elucidation (effect of charge and discharge current, temp, electrolyte conc. on Li dendrite. Surface energy induced Li dendrite growth).
- Mathematical modeling for predicting product performance based on process variables (electron beam polymerizing process, beam dosage, line speed, electrode density, thickness, etc.).

*Altus Corporation, San Jose, CA (Technology: Lithium thionyl chloride, sulfur dioxide, copper chloride batteries)*

**Scientist**

2/1986 – 4/1990

- Awarded 4 patents related to battery technology.
- Worked on Li-SOCl<sub>2</sub> primary, Li-SO<sub>2</sub> primary and Li-CuCl<sub>2</sub> rechargeable cells.
- Studied physical-chemical properties of electrolyte (vapor pressure, conductivity, solubility etc.). Developed tooling for above.
- Developed electrolyte formulation (SO<sub>2</sub>, Cl<sub>2</sub>, SO<sub>2</sub>Cl<sub>2</sub>, anti-passivation additives in SOCl<sub>2</sub>).
- Developed electrolyte drying method (converting -OH, purging) resulting in <20ppm water in electrolyte.
- Conducted routine chemical analysis; significantly improved routine AA method.
- Conduct competitor product analysis (cell tear-down, material characterization etc.)
- Supervised pilot plant operation to produce 200 liter electrolyte per day.

**EDUCATION**

Ph.D., Physical Chemistry, 1985, University of California, Davis, CA

B.S., Agricultural Chemistry, 1976, National Taiwan University, Taiwan

**SPECIALIZED SKILLS**

- Battery technology in general, formulation, processing, testing techniques.
- Electrochemistry: various potentiometric, galvanometric, AC impedance techniques.
- Analytical chemistry and powder characterization: Chromatography, Spectroscopy, Wet chemistry, Particle size analysis, Surface area analysis, DSC, TGA
- Physical chemistry: chemical thermodynamics, kinetics.
- Statistics: experimental design & analysis, inference, optimization, mathematical modeling.



- Chemistry in general: organic, inorganic.
- Mechanical design with SolidWorks, shop operation; Electronic design: analog circuits.
- Computer programming skills: Visual Basic for Excel, esp. for data processing, statistics.

#### **PATENTS/PUBLICATIONS/PROFESSIONAL ASSOCIATIONS**

20 issued patents; 9 publications; numerous corporate & government reports

Member of the Electrochemical Society and the American Chemical Society

#### **PERSONAL**

US citizen since 1992.

#### **PATENTS**

- (1) 4,844,993; Additive to improve voltage regulation in Li-CuCl<sub>2</sub> cell
- (2) 4,863,815; Cell design for spirally wound rechargeable Li metal cell
- (3) 4,873,158; Overdischarge protection for rechargeable cells
- (4) 4,892,796; Positive current collector for lithium secondary cells
- (5) 4,902,588; Additive to improve voltage regulation in Li-CuCl<sub>2</sub> cells
- (6) 5,290,702; Method of mapping organic solvent on a surface
- (7) 5,290,704; Method of detecting organic solvent vapor
- (8) 5,304,436; Method for drying a non-aqueous liquid electrolyte
- (9) 5,326,653; Battery unit with reinforced current collector tabs
- (10) 5,354,631; Enhanced lithium surface
- (11) 5,357,786; Device for determining mechanical properties of material
- (12) 5,390,230; Controlled atmosphere sample holder for x-ray diffraction
- (13) 5,426,055; Method to detect decomposition products in Li salt non-aqueous electrolyte
- (14) 5,438,249; State of charge indication by measuring cell thickness
- (15) 5,442,298; Method for measuring resistivity of geometrically undefined material
- (16) 5,453,261; Method of synthesizing high surface area vanadium oxide
- (17) 5,469,069; Method for measuring resistivity of geometrically undefined material
- (18) 5,520,903; Method of making lithium metal oxide cathode active material
- (19) 5,542,163; Electrically conducting adhesion promoter
- (20) 5,545,496; Method of synthesizing filament-like vanadium oxide for rechargeable cell

#### **PUBLICATIONS**

- (1) C. Cecilio, O. Chang, J. Hall, C. Holloter, J. Morimoto, J. Phillips, and L. Silvester; Performance characteristics of inorganic electrolyte rechargeable cell. Proceedings of the 4th international seminar on lithium batteries. Deerfield Beach, FL; Mar. 1989.
- (2) O. Chang, J. Hall, J. Phillips and L. Silvester; Rechargeable lithium cells with inorganic electrolyte. Proceedings of 33rd international power sources symposium. Electrochemical Society; Cherry Hill, NJ; June 1988.
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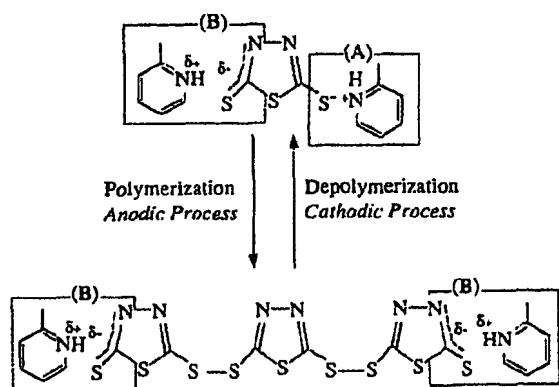


Fig. 5. Proposed structural change of DMcT in PVP film during the oxidation-reduction cycle.

the drawbacks previously mentioned for DMcT electrodes have been overcome by using DMcT/PVP composite films.

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## Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries

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#### ABSTRACT

Reversible extraction of lithium from  $\text{LiFePO}_4$  (triphylite) and insertion of lithium into  $\text{FePO}_4$  at 3.5 V vs. lithium at 0.05 mA/cm<sup>2</sup> shows this material to be an excellent candidate for the cathode of a low-power, rechargeable lithium battery that is inexpensive, nontoxic, and environmentally benign. Electrochemical extraction was limited to ~0.6 Li/formula unit; but even with this restriction the specific capacity is 100 to 110 mAh/g. Complete extraction of lithium was performed chemically; it gave a new phase,  $\text{FePO}_4$ , isostructural with heterosite,  $\text{Fe}_{0.95}\text{Mn}_{0.05}\text{PO}_4$ . The  $\text{FePO}_4$  framework of the ordered olivine  $\text{LiFePO}_4$  is retained with minor displacive adjustments. Nevertheless the insertion/extraction reaction proceeds via a two-phase process, and a reversible loss in capacity with increasing current density appears to be associated with a diffusion-limited transfer of lithium across the two-phase interface. Electrochemical extraction of lithium from isostructural  $\text{LiMPO}_4$  (M = Mn, Co, or Ni) with an  $\text{LiClO}_4$  electrolyte was not possible; but successful extraction of lithium from  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$  was accomplished with maximum oxidation of the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  occurring at  $x = 0.5$ . The  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple was oxidized first at 3.5 V followed by oxidation of the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  couple at 4.1 V vs. lithium. The  $\text{Fe}^{3+}$ -O-Mn<sup>2+</sup> interactions appear to destabilize the  $\text{Mn}^{3+}$  level and stabilize the  $\text{Fe}^{3+}$  level so as to make the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  energy accessible.

#### Introduction

Since the demonstration of reversible lithium intercalation between the layers of  $\text{TiS}_2$ ,<sup>1</sup> considerable effort has been devoted to the identification of other lithium-insertion compounds that can be used as the cathode for a secondary lithium battery. The desired material would have a relatively flat open-circuit voltage over a large lithium solid solution within the voltage range of 2.5 <  $V_{oc}$  < 4.0 V and be inexpensive, easy to fabricate, environmentally

benign, and safe in handling and operation. Reversible lithium insertion/extraction has been performed on a variety of compounds containing different transition-metal cations and structural architectures. The sulfides have too low a  $V_{oc}$  and the halides too low an electronic conductivity, so particular attention has been given to transition-metal oxides. These efforts have resulted in the development of rechargeable lithium batteries that now serve as state of the art power sources for consumer electronics.

Among the known Li-insertion compounds, the layered rock salt systems  $\text{Li}_{1-x}\text{CoO}_2$ ,<sup>2</sup>  $\text{Li}_{1-x}\text{NiO}_2$ ,<sup>3</sup> and the manganese-spinel framework system  $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$ <sup>4</sup> are now

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used commercially as 4.0 V positive-electrode materials in rechargeable lithium batteries. However, the voltages in excess of 4.0 V on higher charge in these oxides can lead to the decomposition of the electrolytes, and the fully charged compounds are metastable:  $[\text{Mn}_2]\text{O}_4$  converts to  $\alpha\text{-MnO}_2$  at 190°C while fully charged phases of  $\text{Li}_{1-x}\text{CoO}_2$  and  $\text{Li}_{1-x}\text{NiO}_2$  lose  $\text{O}_2$  above 180 and 250°C, respectively.<sup>6</sup> Moreover, a lower lithium mobility within the  $[\text{Mn}_2]\text{O}_4$  spinel framework limits its power capability. Although the  $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$  system has a flat  $V_{\text{oc}} \approx 3.0$  V vs. lithium, which is attractive,<sup>7</sup> structural changes associated with a cooperative Jahn-Teller deformation of the framework tend to reduce the capacity irreversibly on repeated cycling.<sup>8</sup> In addition, the availability and cost of the transition metals used in these compounds are unfavorable as the Wh/\$ is a more important figure of merit than Wh/g in the case of large batteries to be used in an electric vehicle or a load-leveling system. These considerations have motivated the investigations of iron-based oxides.

The iron-based oxides containing  $\text{O}^{2-}$  as the anion pose a problem for the cathode designer; in these oxides the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy tends to lie too far below the Fermi energy of a lithium anode and the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple too close to it. Layered  $\text{LiFeO}_2$ , prepared by ion-exchange from  $\alpha\text{-NaFeO}_2$ ,<sup>9</sup> has been investigated.<sup>10</sup> It would operate on the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple, but it is metastable and gives unimpressive battery performance. The other iron-based compounds proposed, viz.  $\text{FePS}_3$ ,<sup>11</sup>  $\text{FeOCl}$ ,<sup>12</sup> and  $\text{FeOOH}$ ,<sup>13</sup> have a relatively poor rechargeability and/or too low a discharge voltage. On the other hand, the use of polyanions such as  $(\text{SO}_3)^{2-}$ ,  $(\text{PO}_3)^{2-}$ ,  $(\text{AsO}_3)^{2-}$ , or even  $(\text{MoO}_3)^{2-}$  or  $(\text{WO}_3)^{2-}$  have been shown to lower the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy to useful levels. Among the compounds with NASICON framework, for example, the open-circuit voltages vs. lithium are 3.0 V for  $\text{Li}_2\text{Fe}_2(\text{SO}_4)_3$ ,<sup>14</sup> 2.8 V for  $\text{Li}_2\text{Fe}_2(\text{PO}_4)_3$ ,<sup>15</sup> and 3.75 V for  $\text{Li}_2\text{Fe}_2\text{Ti}(\text{PO}_4)_3$ ,<sup>16</sup> each of these materials has a specific capacity of about 100 mAh/g. Tuning of the energy of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple is accomplished through the choice of the counteranion within the polyanion. Polarization of the electrons of the  $\text{O}^{2-}$  ions into strong covalent bonding within the polyanion reduces the covalent bonding to the iron ion, which lowers its redox energy. The stronger the covalent bonding within the polyanion, the lower is the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy and the higher the  $V_{\text{oc}}$  vs. lithium for that couple.

The open NASICON framework allows fast  $\text{Li}^+$ -ion diffusion, but a separation of the  $\text{FeO}_6$  octahedra by polyan-

ions reduces the electronic conductivity, which is polaronic in the mixed-valent state. In this paper we report the cathode performance of an iron phosphate having an ordered olivine structure in which the  $\text{FeO}_6$  octahedra share common corners.

The  $\text{M}_2\text{XO}_4$  olivine structure has M atoms in half of the octahedral sites and X atoms in one-eighth of the tetrahedral sites of an hexagonal close-packed (hcp) oxygen array; it is the hexagonal analog of the cubic normal spinel  $\text{X}(\text{M}_2)_4\text{O}_4$ . Olivine crystallizes in preference to spinel for certain small X ions such as  $\text{Be}^{2+}$ ,  $\text{B}^{3+}$ ,  $\text{Si}^{4+}$ ,  $\text{P}^{3+}$ , and occasionally  $\text{Ge}^{4+}$ . Unlike spinel, the two octahedral sites in olivine are crystallographically distinct and differ in size, which favors ordering in  $\text{MM}'\text{XO}_4$  olivines containing M and M' ions of different size and charge. The  $\text{LiMPO}_4$  compounds, with M = Fe, Mn, Co, or Ni, have the ordered olivine structure.

Figure 1 shows the crystal structure of olivine: an ideal hcp model and the actual structure. In the actual structure, the M(1) site has  $\bar{1}$  symmetry, the M(2) octahedron has mirror symmetry with average M-O distances greater than that in the M(1) octahedron. The M(1) sites form linear chains of edge-shared octahedra running parallel to the c-axis in the alternate a-c planes; the M(2) sites form zig-zag planes of corner-shared octahedra running parallel to the c-axis in the other a-c planes (see Fig. 6). Each M(1) site shares its edges with two M(2) sites and two X sites; there is one edge shared by an M(2) site with an X site.<sup>17</sup> Distortion of the hcp oxygen array has been related to the cation-cation coulomb repulsion across the shared edges. In the  $\text{LiMPO}_4$  (M = Mn, Fe, Co, or Ni) compounds, the lithium moieties occupy M(1) sites and the M atoms M(2) sites. With Li in the continuous chain of edge-shared octahedra on alternate a-c planes, a reversible extraction/insertion of lithium from/into these chains would appear to be analogous to the two-dimensional extraction or insertion of lithium in the  $\text{LiMO}_2$  layered oxides with M = Co or Ni. On the other hand, the  $\text{XO}_4$  tetrahedra bridge between adjacent M(2) planes in the olivine structure, which constrains the free volume in which the  $\text{Li}^+$  ions move; only the Li-O bonding constrains the spacing between  $\text{MO}_2$  layers in the  $\text{LiMO}_2$  compounds.

Our attempts to delithiate  $\text{LiMnPO}_4$ ,  $\text{LiCoPO}_4$ , and  $\text{LiNiPO}_4$  proved unsuccessful with the  $\text{LiClO}_4$  electrolyte used. However, we could use our ability to delithiate  $\text{LiFePO}_4$  to initiate delithiation in the solid-solution system  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ; we report a  $\text{Mn}^{3+}/\text{Mn}^{2+}$  couple at

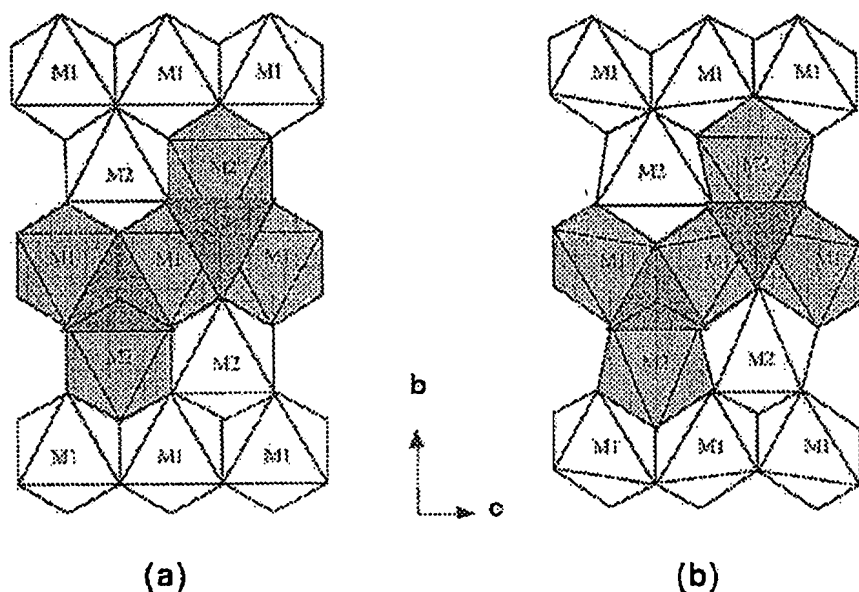


Fig. 1. Olivine crystal structure: (a) ideal HCP model, (b) actual structure.

4.1 eV below the Fermi energy of a lithium anode where there are  $\text{Fe}^{3+}$ -O-Mn $^{3+}$  interactions.

### Experimental

$\text{LiMPO}_4$  ( $M = \text{Mn, Fe, Co, or Ni}$ ) compounds were prepared by direct solid-state reaction of stoichiometric amounts of  $M(\text{II})$ -acetates, ammonium phosphate, and lithium carbonate.  $\text{LiFePO}_4$  and  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$  ( $x = 0.25, 0.50$ , and  $0.75$ ) were synthesized in inert atmosphere to prevent the formation of  $\text{Fe}^{3+}$  compounds as impurities. The intimately ground stoichiometric mixture of the starting materials was first decomposed at 300 to 350°C to drive away the gases. The mixture was then reground and returned to the furnace at 800°C for 24 h before being cooled slowly to room temperature. The x-ray powder diffraction technique was used to identify the phases. The unit-cell parameters were obtained with a least squares refinement to the diffraction peaks. Rietveld refinement of the x-ray diffraction (XRD) data was performed to obtain the structure.

The electrochemical extraction/insertion of lithium and characterization of the performance of the phospho-olivines as cathodes were made with coin-type cells (Type 2320). After the materials were ground to fine particles with a milling machine, they were mixed/blended with acetylene black and polytetrafluoroethylene (PTFE) in the weight ratio 70:25:5. This cathode mixture, after being kept at 140°C for 2 h, was rolled into thin sheets of uniform thickness and cut into pellets of required size for coin-cell fabrication. The electrolyte was 1 M  $\text{LiClO}_4$  in a 1:1 mixture of propylene carbonate (PC) and dimethoxyethane (DME). A lithium foil was used as the anode. The coin cell was fabricated in a glove box under argon atmosphere.

Chemical delithiation to obtain  $\text{Li}_{1-x}\text{MPO}_4$  ( $0 < x < 1$ ) was performed by reacting the materials with nitronium hexafluorophosphate ( $\text{NO}_2\text{PF}_6$ ) in acetonitrile under inert atmosphere. Reaction of  $\text{LiFePO}_4$  with bromine in acetonitrile was also used to extract lithium chemically. Chemical lithiation was carried out by reacting the material with lithium iodide. The products were washed several times with acetonitrile to ensure the purity of the solid phase before it was dried in vacuum. Atomic absorption spectroscopy was performed on intermediate compositions to obtain the exact lithium content with a Perkin-Elmer 1100 spectrometer.

The thermal stability of the phases was monitored from 50 to 500°C by TGA and DSC techniques on a Perkin-Elmer Thermal Analysis 7 instrument. These experiments were performed in both oxygen and an inert atmosphere.

### Results and Discussion

Electrochemical charge and discharge curves for  $\text{LiFePO}_4$ , Fig. 2, show that approximately 0.6 lithium atoms per formula unit can be extracted at a closed-circuit voltage of 3.5 V vs. lithium and the same amount can be reversibly inserted back into the structure on discharge. The extraction and insertion of lithium ions into the structure of  $\text{LiFePO}_4$  is not only reversible on repeated cycling; the capacity actually increases slightly with cycling.

The placement of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy at 3.5 eV below the Fermi level of lithium in  $\text{Li}_{1-x}\text{FePO}_4$  is to be compared with 2.8 eV found<sup>16,18</sup> in  $\text{Li}_{1-x}\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Li}_{1-x}\text{FeTi}(\text{PO}_4)_2$ , and at 3.6 eV in  $\text{Li}_2\text{Fe}_2(\text{SO}_4)_3$ .<sup>14</sup> A difference of 0.8 eV between the redox energies in the isostructural NASICON frameworks of  $\text{Li}_{1-x}\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Li}_2\text{Fe}_2(\text{SO}_4)_3$  can be attributed to the inductive effect, the oxygen forming a stronger bond within  $(\text{SO}_4)^{2-}$  than in  $(\text{PO}_4)^{3-}$  polyanions. On the other hand, all the oxygen of both  $\text{Li}_{1-x}\text{FePO}_4$  and  $\text{Li}_{1-x}\text{Fe}_2(\text{PO}_4)_3$  form strong covalent bonds within a  $(\text{PO}_4)^{3-}$  complex, so the 0.7 eV difference in the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energies of these two compounds must have another origin than the inductive effect. For the origin of this difference, we turn to the ionic component of the bonding.

In an ionic compound, the position of the electron energy levels depends critically on the Madelung potential at the different atoms, which depends on both the structure

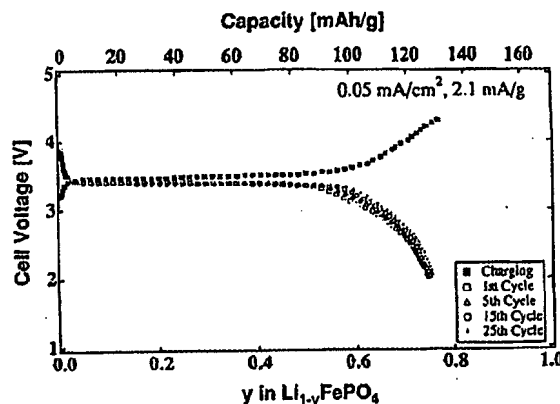
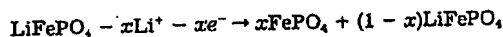


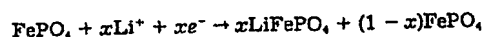
Fig. 2. Discharge/charge curves vs. lithium at 2.0 mA/g ( $0.05 \text{ mA/cm}^2$ ) for  $\text{Li}_{1-x}\text{FePO}_4$ .

and the degree of covalence in the bonding. The Madelung electric field raises the electron energies of the cations and lowers those of anions; in an ionic crystal, the Madelung fields are strong enough to overcome the energy required to create the ionic species, and the redox states are antibonding states of primarily cationic origin. Reference to an  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy implies a substantial ionic component to the bonding; and the stronger the Madelung electric field at the cation site, the higher is the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy. The Madelung sum of coulomb energies can account qualitatively for a lower  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy, and hence a higher  $V_{oc}$  vs. lithium in  $\text{Li}_{1-x}\text{FePO}_4$  than in  $\text{Li}_{1-x}\text{Fe}_2(\text{PO}_4)_3$ . In the NASICON framework, the  $\text{FeO}_6$  octahedra share no edges with other cation polyhedra, which reduces the cation-cation coulomb repulsions contributing to the Madelung sum, whereas considerable edge sharing occurs in the ordered olivines. The cation-cation repulsive forces distort the hcp anion array of an olivine, as noted above, but the repulsion is not sufficient to screen the reduction by these forces of the total Madelung electric field that raises the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox energy above the  $(\text{PO}_4)^{3-}$  energies. Therefore, the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  level lies lower in the ordered olivine structure.

The  $V(x)$  curves for  $\text{Li}_{1-x}\text{FePO}_4$  in Fig. 2 show a voltage that is independent of  $x$  over a large range of  $x$ , which indicates, by Gibbs's phase rule, that the extraction/insertion reactions proceed by the motion of a two-phase interface. To establish the existence and structure of the second phase, a partial chemical delithiation was performed by reacting  $\text{LiFePO}_4$  with varying amounts  $\text{NO}_2\text{PF}_6$  in acetonitrile. Chemical delithiation allows XRD patterns to be taken on clean samples. The XRD patterns in Fig. 3 show the emergence and growth of a second phase at the expense of  $\text{LiFePO}_4$ , as more and more lithium is extracted. With total chemical delithiation, the second phase could be identified by both chemical analysis and Rietveld refinement to XRD data to be  $\text{FePO}_4$ . XRD patterns for chemical lithiation of  $\text{FePO}_4$ , Fig. 4, show the emergence and growth of  $\text{LiFePO}_4$  at the expense of  $\text{FePO}_4$  on more lithiation. Electrochemical characterization of a cathode made from the  $\text{FePO}_4$  obtained by total chemical delithiation of  $\text{LiFePO}_4$  gave the  $V(x)$  curves of Fig. 5; they are similar to those of Fig. 2, thus confirming that  $\text{FePO}_4$  is the second phase that is present on electrochemical extraction of lithium from  $\text{LiFePO}_4$ . Therefore the extraction of lithium from  $\text{LiFePO}_4$  to charge the cathode may be written as



and the reaction for the insertion of lithium into  $\text{FePO}_4$  on discharge as



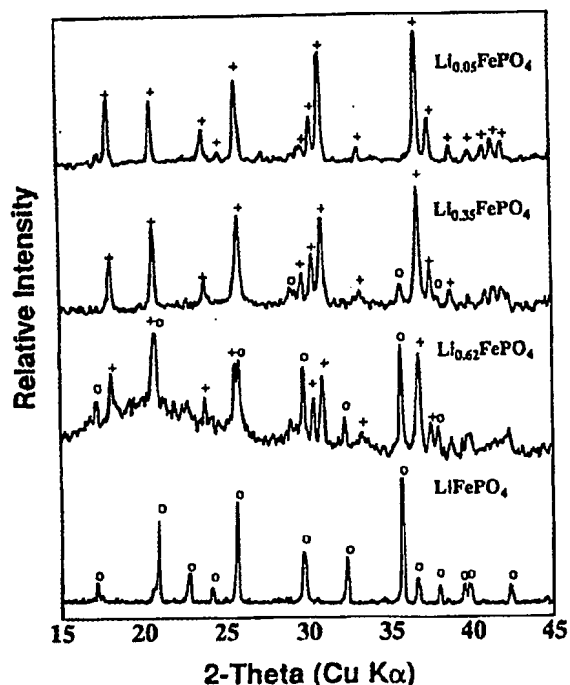


Fig. 3. Chemical delithiation of  $\text{LiFePO}_4$ . XRD patterns showing the emergence and growth of the second phase  $\text{FePO}_4$ .

The excellent reversibility of the cells on repeated cycling is due to the striking similarity of the  $\text{LiFePO}_4$  and  $\text{FePO}_4$  structures, which are compared in Fig. 6.  $\text{FePO}_4$  is isostructural with heterosite,  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{PO}_4$ , for which several bond lengths have been refined.<sup>10</sup> The lattice

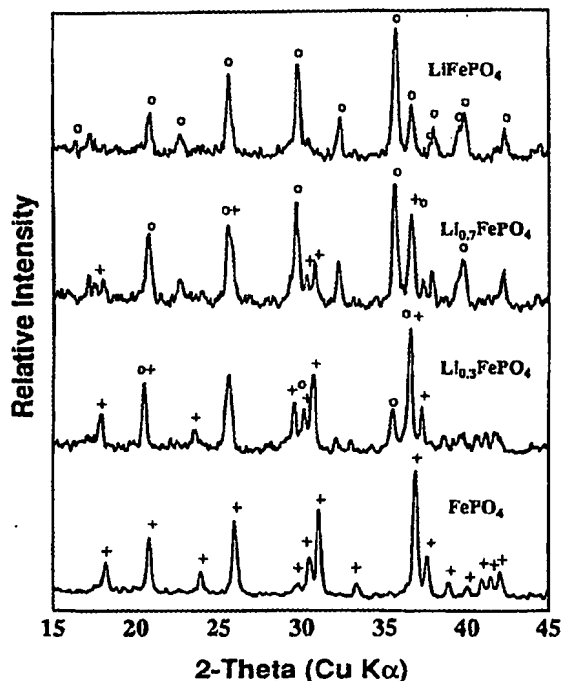


Fig. 4. Chemical lithiation of  $\text{FePO}_4$ . XRD patterns showing the emergence and growth of the second phase  $\text{LiFePO}_4$ .

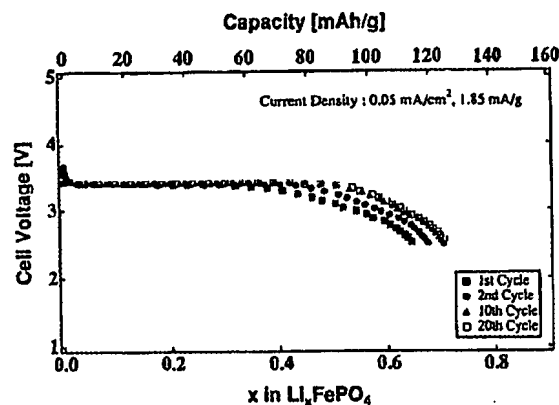


Fig. 5. Discharge/charge curves vs. lithium at 2.0 mA/g ( $0.05 \text{ mA/cm}^2$ ) for  $\text{Li}_x\text{FePO}_4$ .

parameters and the space group of both  $\text{LiFePO}_4$  and  $\text{FePO}_4$  phases are listed in Table I; both  $\text{LiFePO}_4$  and  $\text{FePO}_4$  have the same space group. On chemical extraction of lithium from  $\text{LiFePO}_4$ , there is a contraction of the  $a$  and  $b$  parameters, but a small increase in the  $c$  parameter. The volume decreases by 6.81% and the density increases by 2.59%. Although the changes in the  $\text{FePO}_4$  framework are displacive, not diffusional, a first-order transition between  $\text{LiFePO}_4$  and  $\text{FePO}_4$  prevents the continuous insertion reaction

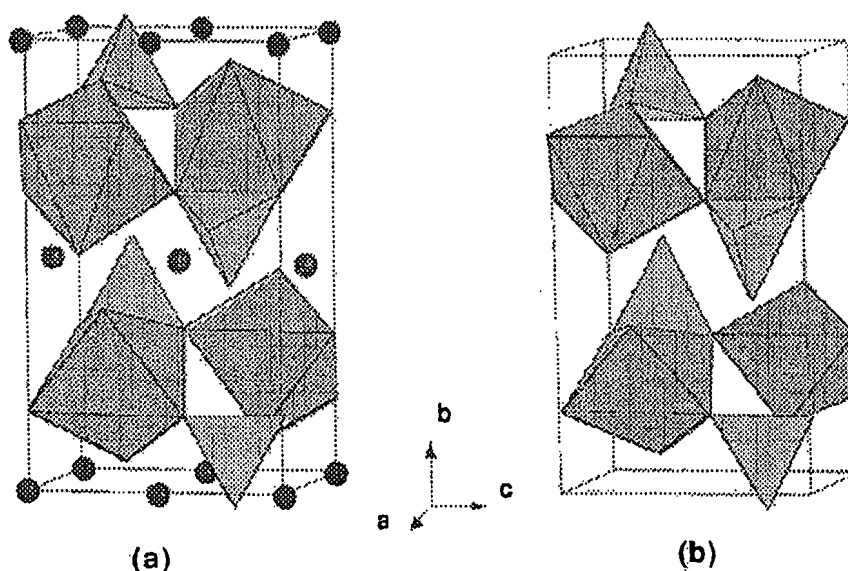


A first-order transition would seem to require a cooperative elastic deformation of the  $\text{FePO}_4$  framework. It is therefore of interest that the principal change in the framework on delithiation is a cooperative adjustment of the framework to the coulombic repulsion between the  $\text{O}^{2-}$  ion sheet interfacing the delithiated planes.

Insertion of lithium into  $\text{FePO}_4$  was reversible over the several cycles investigated.  $\text{Li}_x\text{FePO}_4$  represents a cathode of good capacity, and it contains inexpensive, environmentally benign elements. However, a nearly close-packed hexagonal oxide-ion array that is bonded strongly in three dimensions provides a relatively small free volume for  $\text{Li}^+$  ion motion, so the electrode supports only relatively small current densities at room temperature. Nevertheless, increasing the current density does not lower the open-circuit voltage  $V_{oc}$ ; rather it decreases, reversibly, the cell capacity. Reducing the current restores the capacity. This observation indicates the loss in capacity is a diffusion-limited phenomenon associated with the two-phase character of the insertion process.

As is illustrated schematically in Fig. 7, lithium insertion proceeds from the surface of the particle moving inward behind a two-phase interface, a  $\text{Li}_x\text{FePO}_4/\text{Li}_{1-x}\text{FePO}_4$  interface in this system. As the lithiation proceeds, the surface area of the interface shrinks. For a constant rate of lithium transport per unit area across the interface, a critical surface area is reached where the rate of total lithium transported across the interface is no longer able to sustain the current; the cell performance becomes diffusion-limited. The higher the current, the greater is the total critical interface area and, hence, the smaller the concentration  $x$  of inserted lithium before the cell performance becomes diffusion-limited. On extraction of lithium, the parent phase at the core of the particle grows back toward the particle surface, which is why the parent phase is retained on repeated cycling and the loss in capacity is reversible on lowering the current density delivered by the cell. This loss of capacity is not due to a breaking of the electrical contact between particles as a result of volume changes, a process that is normally irreversible.

Fig. 6. Crystal structures of (a)  $\text{LiFePO}_4$  and (b)  $\text{FePO}_4$ .



The thermal stability of the fully charged state of  $\text{LiFePO}_4$ ,  $\text{FePO}_4$ , is shown in the TGA curves of Fig. 8. On thermal treatment of  $\text{FePO}_4$  in nitrogen atmosphere up to  $350^\circ\text{C}$ , there was no appreciable change in the weight. A weight loss of 1.6% is observed when the sample was heated up to  $500^\circ\text{C}$ . There was very little difference in the TGA curves when the sample was heated in oxygen atmosphere. No appreciable change could be found in the XRD patterns taken after thermal treatment; there was no trace of impurity. Since the  $\text{FePO}_4$  for these experiments was prepared by treating  $\text{LiFePO}_4$  with bromine several times in acetonitrile, there could be a small amount of  $\text{LiBr}$  in the sample even after washing the products several times with acetonitrile, which decomposes at  $350^\circ\text{C}$ . The DSC curve shows a small reversible peak at  $300^\circ\text{C}$  of unknown origin.

In order to locate the  $\text{Mn}^{3+}/\text{Mn}^{2+}$ ,  $\text{Co}^{3+}/\text{Co}^{2+}$ , and  $\text{Ni}^{3+}/\text{Ni}^{2+}$  redox energies with respect to the Fermi energy of lithium, we tried to extract lithium electrochemically from other  $\text{LiMPO}_4$  compounds with  $M = \text{Mn}, \text{Co},$  or  $\text{Ni}$ . Since  $\text{LiClO}_4$  with 1:1 by volume mixture of PC and DME was used as the electrolyte, the upper voltage limit used in our experiments were 4.3 to 4.4 V. Higher upper voltages resulted in oxidation of the electrolyte, and we could not initiate access to the  $\text{Mn}^{3+}/\text{Mn}^{2+}$ ,  $\text{Co}^{3+}/\text{Co}^{2+}$ , and  $\text{Ni}^{3+}/\text{Ni}^{2+}$  redox couples in these compounds. However, we could access the  $\text{Mn}^{3+}/\text{Mn}^{2+}$  couple in the presence of some iron atoms in the structure. Solid-solutions  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$  with  $x = 0.25, 0.50,$  and  $0.75$  were synthesized. Figure 9 shows linear increases of the lattice parameters with increasing Mn content in the structure, in accordance with Vegard's law.

Figure 10a-d show the electrochemical charge and discharge curves for coin-type cells with  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$  ( $x = 0.25, 0.50, 0.75,$  and  $1.0$ ) as the cathode and lithium as the anode. The charging curve for  $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ , Fig. 10a, shows a small plateau at 4.1 V, which is not very distin-

guishable in the discharge curve. For  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ , the charging curve Fig. 10b shows two distinct plateaus of almost equal width, and these plateaus are reproducible on discharge and over repeated cycling. As the Mn content is increased in the structure, the amount of lithium that can be electrochemically extracted by charging decreases as is evident in Fig. 10c for  $\text{LiFe}_{0.25}\text{Mn}_{0.75}\text{PO}_4$ . With all the Fe atoms replaced by Mn atoms as in  $\text{LiMnPO}_4$ , lithium could not be extracted either electrochemically, Fig. 10d, or chemically by reacting with  $\text{NO}_2\text{PF}_6$  in acetonitrile.

From these observations, we conclude that the  $\text{Mn}^{3+}/\text{Mn}^{2+}$  redox couple in phospho-olivines lies 4.1 eV below the Fermi energy of lithium if the Mn atoms have an Fe atom as a nearest neighbor. Destabilization in the presence of iron of the  $\text{Mn}^{3+}/\text{Mn}^{2+}$  redox couple from over 4.3 to 4.1 eV below the Fermi energy of lithium could reflect the  $\text{Fe}^{3+}-\text{O}-\text{Mn}^{2+}$  superexchange interaction; the  $\text{Mn}^{2+}$  level would be antibonding and the  $\text{Fe}^{3+}$  level bonding with respect to this interaction. In  $\text{LiMPO}_4$  with  $M = \text{Co}$  and  $\text{Ni}$ , the  $\text{M}^{3+}/\text{M}^{2+}$  redox energies lie well below the highest occupied molecular orbital of our electrolyte, with the  $\text{Ni}^{3+}/\text{Ni}^{2+}$  redox couple lying around 0.6 eV below the  $\text{Co}^{3+}/\text{Co}^{2+}$  redox couple as in the case of the inverse spinels  $\text{V}[\text{LiM}]\text{O}_4$ .

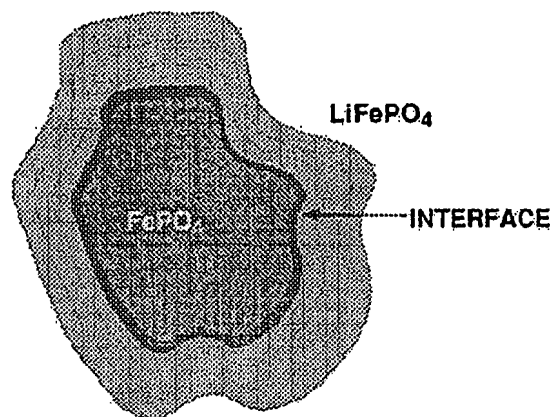


Fig. 7. Schematic representation of the motion of  $\text{LiFePO}_4/\text{FePO}_4$  interface on lithium insertion to a particle of  $\text{FePO}_4$ .

Table I. The space group and lattice parameters of  $\text{LiFePO}_4$  and delithiated phase  $\text{FePO}_4$ .

	$\text{LiFePO}_4$	$\text{FePO}_4$
Space Group	Pb nm	Pb nm
a (Å)	0.008 (3)	5.592 (1)
b (Å)	10.334 (4)	9.821 (1)
c (Å)	4.693 (1)	4.788 (1)
Volume (Å <sup>3</sup> )	291.392 (3)	272.357 (1)

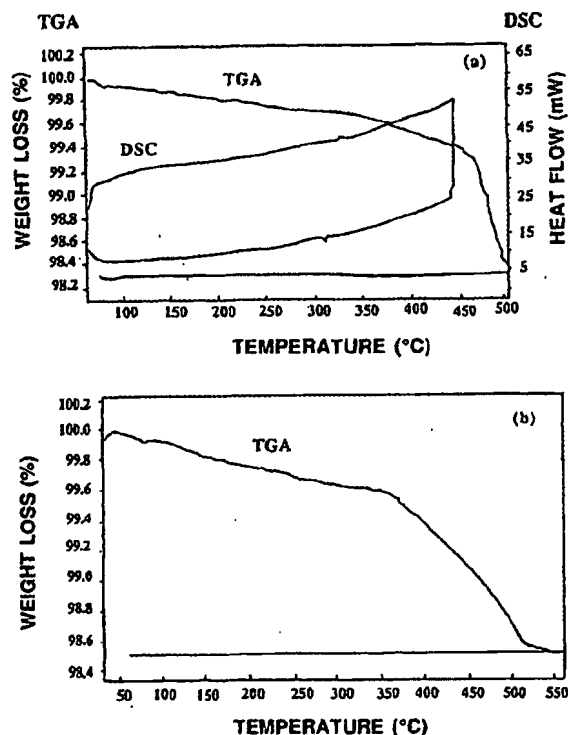


Fig. 8. The thermal stability of delithiated phase FePO<sub>4</sub>: (a) TGA and DSC curves in nitrogen atmosphere and (b) TGA curve in oxygen atmosphere.

with  $M = \text{Co}$  or  $\text{Ni}$ .<sup>18</sup> It appears that the greater covalence of the PO<sub>4</sub> tetrahedron relative to that of the VO<sub>4</sub> tetrahedron not only favors the olivine as against the spinel structure; it also stabilizes the redox couples at the octahedral sites by at least 0.4 eV, lowering the Mn<sup>3+</sup>/Mn<sup>2+</sup> couple from 3.7 eV below the lithium-anode Fermi energy in V[LiMn]O<sub>4</sub> to 4.1 eV in LiFe<sub>0.6</sub>Mn<sub>0.4</sub>PO<sub>4</sub>.<sup>20</sup>

### Conclusion

On extraction of lithium from LiFePO<sub>4</sub>, a flat closed-circuit voltage (CCV) curve at 0.05 mA/cm<sup>2</sup> of 3.5 V vs. lithium is obtained for the Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couple due to the presence of two phases, LiFePO<sub>4</sub> and FePO<sub>4</sub>. These phases belong to the same space group with a variation of the FePO<sub>4</sub> host only in the unit-cell parameters. This material is very good for low-power applications; at higher current densities there is a reversible decrease in capacity that, we suggest, is associated with the movement of a two-phase interface, a feature characteristic of cathodes that traverse a two-phase compositional domain in the discharge cycle. The intercalation of only 0.6 Li atom/formula unit of LiFePO<sub>4</sub> may be an extrinsic problem since the same  $V(x)$  curves are obtained starting with FePO<sub>4</sub>, and essentially all the lithium can be extracted chemically from LiFePO<sub>4</sub>.

The deintercalation of lithium from the solid solution LiFe<sub>1-x</sub>Mn<sub>x</sub>PO<sub>4</sub> ( $x = 0$  to 1) allows location of the position of the Mn<sup>3+</sup>/Mn<sup>2+</sup> redox couple. When  $x = 0$ , we get a plateau at 3.5 V; but as the manganese content is increased, a plateau at 4.1 V appears. Maximum charging at 4.1 V is accomplished for  $x = 0.5$ . As expected, we observe that the oxidation of Mn<sup>2+</sup> occurs only after the oxidation of Fe<sup>2+</sup>. We were unable to take out any lithium from LiMnPO<sub>4</sub>, while charging up to 4.3 V. Moreover, the width of the 4.1 V plateau decreases with increasing  $x > 0.5$ , which suggests that the 4.1 V plateau is associated with the Mn atoms having Fe near neighbors. It appears that the Mn-O-Fe interactions raise the energy of the

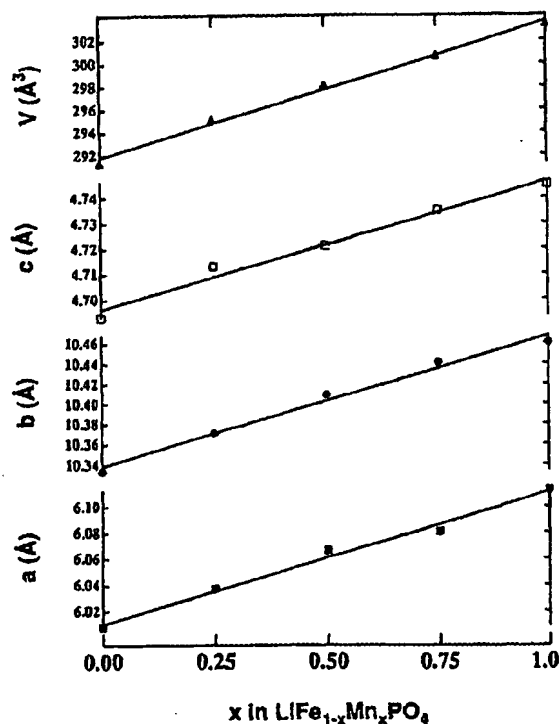


Fig. 9. Variation of lattice parameters of LiFe<sub>1-x</sub>Mn<sub>x</sub>PO<sub>4</sub> with increasing Mn content in the structure.

Mn<sup>3+</sup>/Mn<sup>2+</sup> couple and slightly lower the Fe<sup>3+</sup>/Fe<sup>2+</sup> couple. We were unable to extract Li from isostructural LiCoPO<sub>4</sub> and LiNiPO<sub>4</sub> with the electrolyte LiClO<sub>4</sub> in PC and DME due to the stability of the Co<sup>3+</sup>/Co<sup>2+</sup> and Ni<sup>3+</sup>/Ni<sup>2+</sup> couples.

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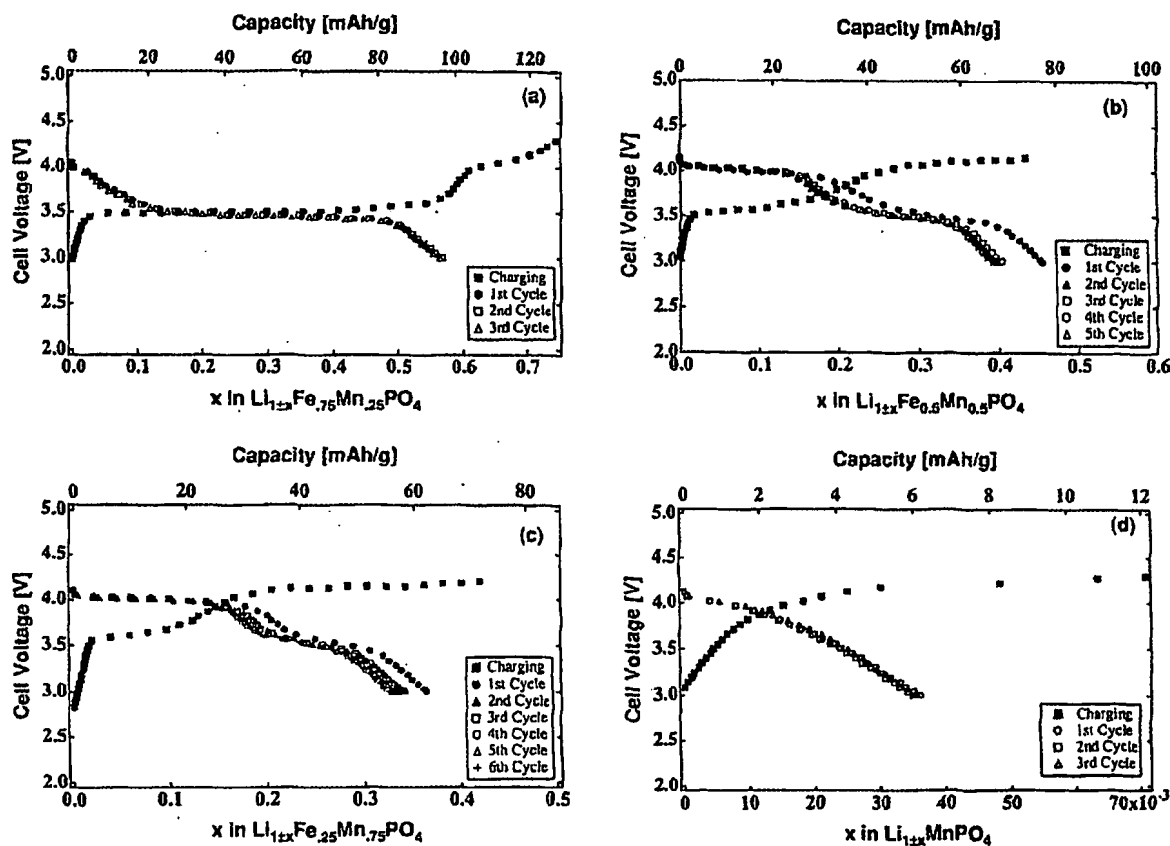


Fig. 10. Discharge/charge curves vs. lithium at current densities 2.0 mA/g, (0.05 mA/cm<sup>2</sup>) for (a) LiFe<sub>0.75</sub>Mn<sub>0.25</sub>PO<sub>4</sub>, (b) LiFe<sub>0.5</sub>Mn<sub>0.5</sub>PO<sub>4</sub>, (c) LiFe<sub>0.25</sub>Mn<sub>0.75</sub>PO<sub>4</sub>, and (d) LiMnPO<sub>4</sub>.

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## EVIDENCE APPENDIX

5. Delacourt et al., "Size Effects on Carbon-Free  $\text{LiFePO}_4$  Powders," *Electrochemical and Solid-State Letters*, 9(7) A352-A355 (2006).



## Size Effects on Carbon-Free LiFePO<sub>4</sub> Powders

### The Key to Superior Energy Density

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C-free LiFePO<sub>4</sub> crystalline powders were prepared by a synthesis method based on direct precipitation under atmospheric pressure. The particle size distribution is extremely narrow, centered on ca. 140 nm. A soft thermal treatment, typically at 500°C for 3 h under slight reducing conditions was shown to be necessary to obtain satisfactory electrochemical Li<sup>+</sup> deinsertion/insertion properties. This thermal treatment does not lead to grain growth or sintering of the particles, and does not alter the surface of the particles. The electrochemical performances of the powders obtained by this synthesis method are excellent, in terms of specific capacity (147 mAh g<sup>-1</sup> at 5C-rate) as well as in terms of cyclability (no significant capacity fade after more than 400 cycles), without the need of carbon coating.

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Olivine-type LiFePO<sub>4</sub>, namely, triphylite, was first proposed by Padhi et al. in 1997 to be used as a positive electrode material for Li-ion batteries.<sup>1</sup> Li<sup>+</sup> deinsertion/insertion of this compound occurs at a potential value of ca. 3.45 V vs Li<sup>+</sup>/Li with a high theoretical specific capacity of 171 mAh g<sup>-1</sup>. The main drawback of this cheap and nontoxic material is its low gravimetric density besides a poor electrical conductivity which limits the Li<sup>+</sup> deinsertion/insertion rates, and hence the practical specific capacity. To overcome this problem, several chemical routes so as to produce carbon coatings at the surface of LiFePO<sub>4</sub> particles were proposed.<sup>2</sup> Besides increasing the overall conductivity of the material through an electronic percolating network around the particles, one generally agrees that such coating also prevents particle growth and sintering during annealing treatments.<sup>3-6</sup>

The presence of carbon has a dramatic impact though on the tap density of the powder: it is reduced by 2 when only 2 wt % carbon is present in the composite material, which gives energy densities only half of those of standard materials such as LiCoO<sub>2</sub>.<sup>7</sup> Moreover, a recent comparative electrochemical study and kinetic modeling of LiFePO<sub>4</sub> powders from different sources concluded that the average particle size of the materials, as well as their distribution (namely, the psd), must be narrowed in order to obtain an ideal material.<sup>8</sup>

AC and dc conductivity measurements of C-free LiFePO<sub>4</sub> dense pellets suggest that carbon coating is far from being the only route to explore for producing a more efficient LiFePO<sub>4</sub> electrode. Li<sup>+</sup> conductivity is indeed likely to be in the same order of magnitude or even lower than the electronic one.<sup>9</sup> A recent DFT contribution of Maxisch et al. confirms our experimental data, as a transport mechanism involving (Li<sub>Li</sub><sup>+</sup>, e<sub>Fe</sub><sup>-</sup>) and (□<sub>Li</sub><sup>+</sup>, h<sub>Fe</sub><sup>+</sup>) exciton-like quasi particles (in FePO<sub>4</sub> and LiFePO<sub>4</sub>, respectively) is envisaged.<sup>10</sup> Limitations appear then to be both ionic and electronic which strengthen the importance of tailoring as small particles as possible so as to shorten both electronic and ionic paths within the particles.

Along that line, Chimie douce is a well-known method to prepare materials having controlled particle size with narrow size distributions. Among the numerous recent contributions on the precipitation of iron-based nanocompounds, one may quote nano-Fe<sub>3</sub>O<sub>4</sub> and nano-Fe<sub>2</sub>O<sub>3</sub>,<sup>11,12</sup> nanoparticles of amorphous hydrated iron phosphates of formula FePO<sub>4</sub>·nH<sub>2</sub>O.<sup>13</sup> Regarding LiFePO<sub>4</sub>, soft chemistry has been restricted so far to the precipitation under hydrothermal conditions.<sup>14-22</sup> Tajimi and Nussli demonstrated first that carbon coating was not any longer essential for providing good elec-

trochemical activity: through the use of surfactants such as PEG, carbon-free LiFePO<sub>4</sub> particles ranged between 0.5 and 1.5 μm with a specific capacity of 140 mAh g<sup>-1</sup> at a current density of 0.5 mA cm<sup>-2</sup>.<sup>20</sup> Nussli et al. reported on a carbon-free powder with a narrow particle size distribution (average in the 400 to 600 nm range) that could deliver 114 mAh g<sup>-1</sup> at 8C rate.<sup>17-19</sup>

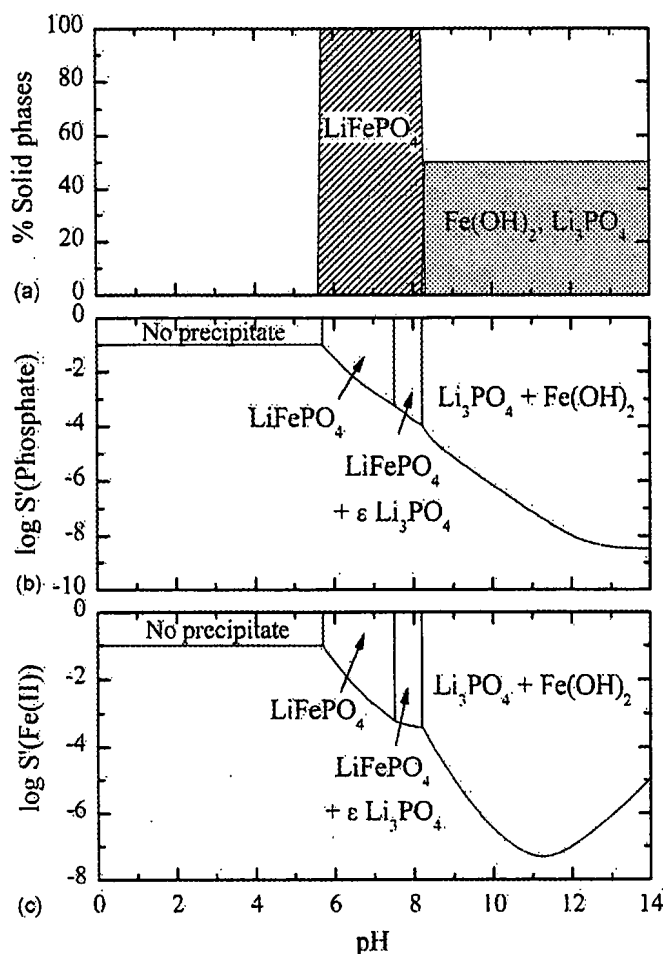
### Experimental

Based on our recent findings on the direct precipitation of crystalline LiMnPO<sub>4</sub> with particle size around 100 to 150 nm, under atmospheric conditions,<sup>23</sup> we used a similar approach for the synthesis of carbon-free LiFePO<sub>4</sub> particles at low temperature under atmospheric pressure.<sup>24</sup> To this end, we first undertook a detailed thermodynamic study of the Li<sup>+</sup>/Fe(II)/phosphate/H<sub>2</sub>O system following our extensive previous studies on the precipitation of FePO<sub>4</sub>·2H<sub>2</sub>O allotropes.<sup>25</sup> Precipitation of LiFePO<sub>4</sub> may occur at an optimal pH value close to neutrality as plotted in the solubility-pH diagram shown in Fig. 1. A mixture of 0.1 mol L<sup>-1</sup> of Fe(II) sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O, Sigma Aldrich) and 0.1 mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> (Baker) was neutralized to this average pH value by slowly adding 0.3 mol L<sup>-1</sup> of LiOH (LiOH·H<sub>2</sub>O, Alfa Aesar), leading to a green mixture which was subsequently kept under refluxing conditions for ca. 16 h under magnetic stirring. The green-grayish precipitate thus obtained was then recovered by centrifugation, washed several times with distilled water and acetone and finally dried in an oven at 50°C for one day (Fig. 2). For electrochemical measurements, the precipitate was previously annealed for 3 h at 500°C under a N<sub>2</sub>/H<sub>2</sub> gas flow in order to fully dehydrate the material and reduce the possible Fe(III)-containing impurities.

X-ray diffraction (XRD) experiments were performed on a Philips PW 1710 diffractometer (θ-2θ, Cu Kα radiation, back monochromator). Powders' morphology was observed by scanning electron microscopy (SEM) by means of a Philips FEG XL-30 and by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) by using a FEI Technai F20 S-Twin. Particle size distribution (psd) was determined from image analysis of SEM pictures of the LiFePO<sub>4</sub> powder. Electrochemical lithium deinsertion/insertion tests were performed either in Swagelok-type cells or in coin cells, which were both assembled in an argon-filled dry box. The negative electrode was a disk of lithium metal foil. A Whatman GF/D borosilicate glass fiber sheet, soaked with a 1 M LiPF<sub>6</sub> salt dissolved in 1:1 EC/DMC solution (Merck, LP30), was placed between the two electrodes. The positive electrodes simply consisted in a mixture of the C-free LiFePO<sub>4</sub> obtained from the precipitation and ketjen black carbon (EC-600 JD, Akzo Nobel), by means of a mortar and a pestle. When used in a Swagelok, the positive electrode

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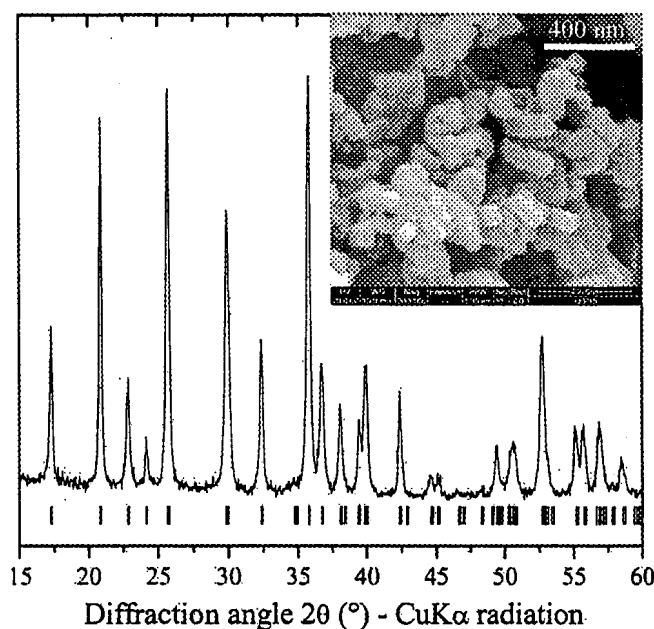


**Figure 1.** (a) Distribution diagram of solid compounds in equilibrium with the solution (molar ratio). (b) Solubility diagram of phosphate. (c) Solubility diagram of Fe(II). Conditions:  $[\text{Fe(II)}]_{\text{tot}} = [\text{Phosphate}]_{\text{tot}} = 0.1 \text{ M}$ ,  $[\text{Li}^+] = 1 \text{ M}$ , an hypothetical  $\text{pK}_s$  value of 12 was chosen for  $\text{LiFePO}_4$ .

material thus obtained was directly led onto the current collector (typical loading of  $\sim 14 \text{ mg}$  for  $1.3 \text{ cm}^2$  current collector area). For coin cells, a slurry of the electrode material and *N*-methylpyrrolidone (NMP) was made and deposited onto the current collector. The electrodes were left for at least 3 h in an oven at  $100^\circ\text{C}$  in order to fully evaporate the NMP. The typical loading in this case was comprised between 2 and 5 mg (for  $1.9 \text{ cm}^2$  current collector area). Lithium deinsertion/insertion was monitored either with MacPile or VMP cycling/data recording systems (Biologic SA, Claix, France), operating in galvanostatic mode.

### Results and Discussion

The XRD pattern of the precipitate obtained for 16 h aging under refluxing conditions is given in Fig. 2. It was entirely indexed in the space group  $Pnma$  reported for  $\text{LiFePO}_4$  (ICSD no. 200155) with lattice constants  $a = 10.294(2) \text{ \AA}$ ,  $b = 5.974(1) \text{ \AA}$ , and  $c = 4.694(1) \text{ \AA}$ , i.e., smaller than usually encountered for  $\text{LiFePO}_4$  prepared through more classic ceramic routes. We do not know yet what is at the exact origin of such behavior. Unlike  $\text{LiMnPO}_4$ ,<sup>23</sup> the nucleation and growth of the olivine-type phase  $\text{LiFePO}_4$  occurs very quickly as crystalline samples were obtained after as small as 15 min under refluxing conditions. The nucleation step is thus likely to be predominant over the growth, which leads to very small particle size comprised between 100 and 200 nm, as illustrated in the inset of Fig. 2.



**Figure 2.** XRD diagram of the as-obtained precipitate after 16 h of reaction under refluxing conditions. Inset: SEM image of the particles, having size comprised between 100 and 200 nm.

Prior to perform electrochemical characterizations of the  $\text{LiFePO}_4$  powder, a heat-treatment under reducing conditions (typically a  $\text{N}_2/10\% \text{ H}_2$  gas flow) was ensured so as to reduce the small amount of Fe(III) together with the removal of parasitic "OH" groups through water departure. Indeed, Mössbauer spectroscopy revealed that the pristine  $\text{LiFePO}_4$  powders may contain up to 15–20 atom % of Fe(III). The presence of O-H groups was attested by Fourier transform (FTIR) measurements: a weak absorption band was detected at  $\sim 3270 \text{ cm}^{-1}$  and was related to O-H bond stretching into the amorphous  $\text{LiFePO}_4(\text{OH})$  phase, from a comparison with the FTIR spectrum of crystalline  $\text{LiFePO}_4(\text{OH})$  (Tavorite, ICDD no. 41-1376) (not shown here). This also suggests that slight amounts of amorphous  $\text{LiFePO}_4(\text{OH})$  composition are present within the powder, which is concordant with the presence of Fe(III). Figures 3a and b are SEM and TEM micrographs of a  $\text{LiFePO}_4$  sample heat-treated at  $500^\circ\text{C}$  for 3 h under  $\text{N}_2/10\% \text{ H}_2$  gas flow. Note that the temperature and the dwell time of the thermal treatment are significantly reduced compared to a ceramic synthesis process. Coarsening of  $\text{LiFePO}_4$  particles is hence significantly reduced, and the average particle size remains in the range of 100–200 nm. Note, however, that the particle morphology has changed during the thermal treatment, from parallelepipeds for the as-made precipitate to spheres for the annealed powders. From SEM analyses, the particle size distribution (psd) could be determined (Fig. 3c). The  $d_{50}$  value is  $\sim 140 \text{ nm}$ , while the relative span, defined as  $(d_{90}-d_{10})/d_{50}$ , is about 0.50. The psd is much narrower and shifted toward smaller values than that reported by Nuspl et al. for  $\text{LiFePO}_4$  hydrothermally synthesized.<sup>17,18</sup>

Surface reactivity is generally enhanced for divided powders, especially during thermal treatments. To identify the possible existence of parasitic phases such as iron phosphides at the surface of the heat-treated  $\text{LiFePO}_4$  powders, HRTEM observations coupled with EDX analyses in STEM mode across  $\text{LiFePO}_4$  particles were carried out (not shown here). The absence of any amorphous layer at the surface of the particles together with the constancy of the Fe/P atomic ratio from the particle core to the surface clearly accounts for the absence of an iron phosphide layer around the particles. This conclusion was strengthened by ac conductivity measurements on dense sintered pellets of the material which show that the electrical

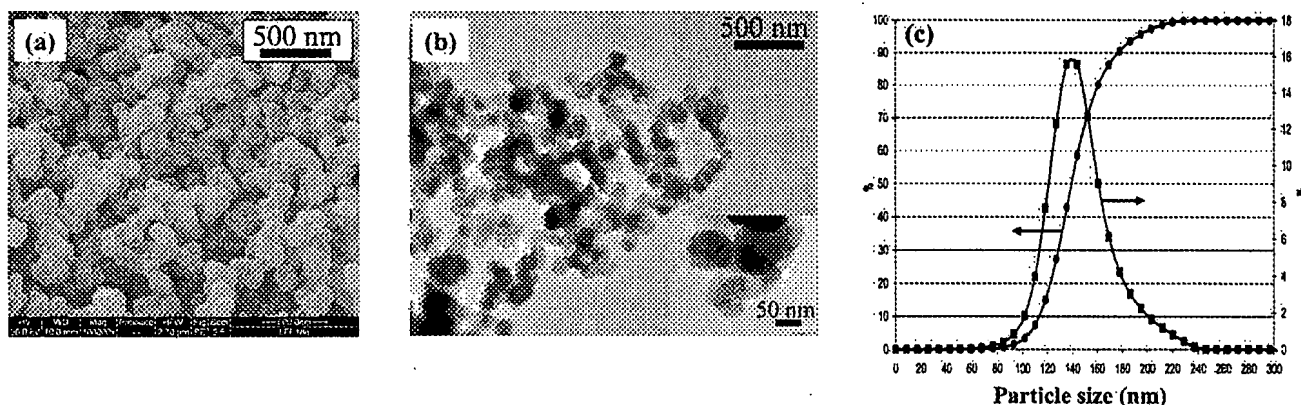


Figure 3. (a) SEM, (b) TEM, and (c) volumetric particle size distribution (obtained from image analysis of SEM images) of the C-free  $\text{LiFePO}_4$  powder obtained after a heat-treatment at  $500^\circ\text{C}$  under  $\text{N}_2/10\% \text{H}_2$  atmosphere for 3 h.

conductivity value of the bulk is comparable to that reported in Ref. 9 for pure  $\text{LiFePO}_4$ , prepared through a ceramic route (not shown here).

As shown in Fig. 4,  $\text{Li}^+$  deinsertion/insertion of the  $\text{LiFePO}_4$  powder mixed with only 5 wt % of ketjen black carbon proceeds with an extremely small polarization, even under high current rates (C/2 during discharge), leading to a high reversible specific capacity of ca.  $145 \text{ mAh g}^{-1}$ . This excellent performance is mostly due to the lowering of the particle size, and hence we wish to stress that carbon coating is no longer required for such a divided material. Note also that no significant capacity fade was observed, even after more than 400 charge/discharge cycles: this may be due to the observed fact that  $\text{LiFePO}_4$  particles are highly monodisperse (very narrow psd centered on 140 nm) leading to an homogeneous current distribution within the electrode. Figure 5 shows signature curves obtained by varying several parameters, such as the amount of carbon in the positive electrode, as well as the type of positive electrode and cell configuration used. At low charge/discharge rates, an increase of the carbon amount from 5 to 16.7% leads to a constant increase of the specific capacity of  $\sim 15 \text{ mAh g}^{-1}$ , whatever the C-rate used. For higher charge/discharge rates (typically  $>1 \text{ C}$  for cells made with powders), the influence of the carbon amount becomes more important. Even at 5 C rate, discharge specific capacities as high as 135

and  $147 \text{ mAh g}^{-1}$  are obtained for  $\text{LiFePO}_4$  electrodes made from NMP-based slurries, and containing 5 and 16.7 wt % ketjen black carbon, respectively.

### Conclusion

A soft chemistry method allowed the preparation of C-free  $\text{LiFePO}_4$  particles in the range 100–200 nm, with a very narrow particle size distribution. This material, after a heat-treatment under slightly reducing conditions, exhibits very satisfactory electrochemical properties in terms of specific capacity and capacity retention upon cycling. These properties are directly linked to the small particle size, which lowers both ionic and electronic transport within the particles. The performances reported here, in terms of specific capacity related to the active material, are identical or slightly higher than those reported for C-coated  $\text{LiFePO}_4$ .<sup>3,5,26</sup> They are therefore superior in terms of energy density due to the absence of C-coating. To conclude, besides being very attractive on a practical aspect,  $\text{LiFePO}_4$ -type electrodes bring us new insights about the importance of size effects on the electrochemical activity. By transposing the same concepts to more insulating materials such as  $\text{LiMnPO}_4$ , one would expect that a huge decrease of the particle size should be the key point for an enhancement of its electrochemical activity.

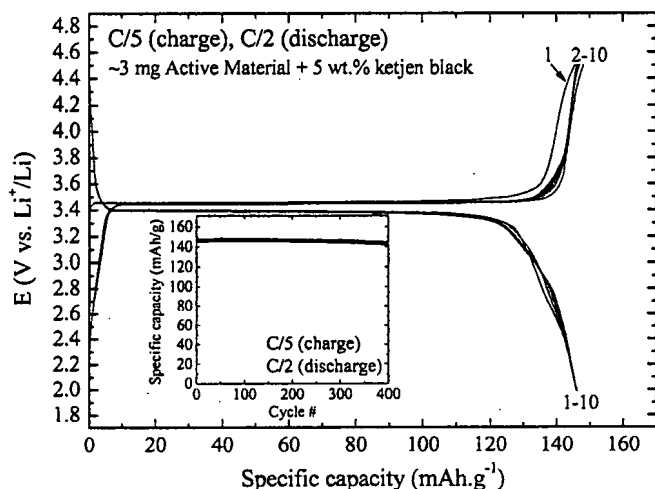


Figure 4. Galvanostatic charge/discharge profiles at  $20^\circ\text{C}$  of an electrode composed of C-free  $\text{LiFePO}_4$  (heat-treated powder) mixed with 5 wt % of ketjen black carbon. The charge rate ( $1 \text{ e}^-$  per formula unit exchanged in 5 h) is lower than of discharge ( $1 \text{ e}^-$  per formula unit exchanged in 2 h). Inset: Specific capacity retention of the active material.

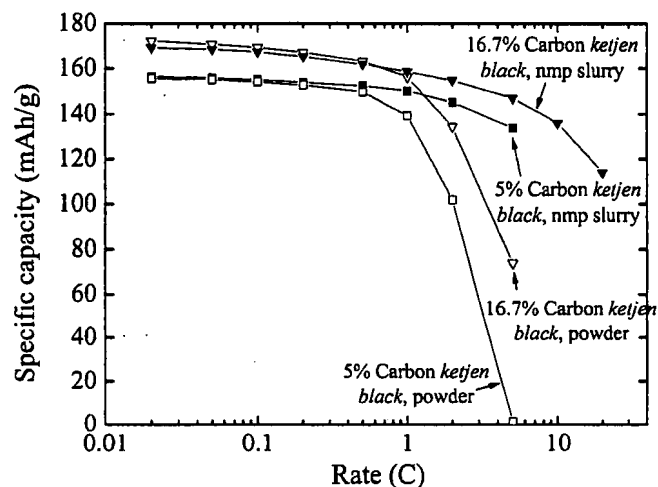


Figure 5. Evolution of the specific capacities relative to the active material as a function of C-rate, at  $20^\circ\text{C}$ . Electrodes made from NMP slurries are composed of  $\sim 3 \text{ mg}$  of active material + ketjen black carbon and are cycled in coin cells. Electrodes directly made from powders of AM + ketjen black carbon are loaded with  $\sim 14 \text{ mg}$  and are cycled in Swagelok-type cells.

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## EVIDENCE APPENDIX

6. U.S. Patent 5,910,382 to Goodenough et al.

## EVIDENCE APPENDIX

7. U.S. Patent 5,849,827 to Bodiger et al.

EVIDENCE APPENDIX

8. U.S. Patent 5,952,125 to Bi et al.